CATHODIC REDUCTION STUDIES.

A Thesis

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S U M M A R Y

The work on which this thesis is based has consisted, in the main, of the study of the reduction of aromatic organic compounds at mercury cathodes. The polarograph has been used to obtain energy quantities which have been related to the structure and electronic distribution of the molecules studied. The use of two non-aqueous solvents, glacial acetic acid and ethylene glycol mono-methyl ether, as polarographic solvents has been extended. The technique of reduction at controlled potential has been used to investigate reduction mechanisms, and for the preparation of air-sensitive material.

The first part of the work consists of the investigation of the polarography of some nitro compounds in glacial acetic acid. This solvent is of interest because it provides an acidic medium in which a large number of organic compounds are soluble, and because of its comparatively high decomposition potential. A series of nitro compounds was studied because of the special interest of the reduction of the nitro group in a medium of constant acidity function. The influence of substituents on the ease of reduction is discussed and results shown to be in general agreement with accepted views on their polar effects.

(A reprint of the paper in the Transactions of the

Faraday Society describing this work is included in the Appendix.)

The reduction states of some nitro compounds and related substances were studied by coulometric reduction at a controlled potential using a stirred mercury cathode. The results, given in Part 2, agree substantially with those obtained by polarography, both in aqueous media and in concentrated sulphuric acid, and glacial acetic acid.

In order to clarify the part played by phenyl-hydroxylamine in the polarographic reduction of nitrobenzene, phenylhydroxylamine has been prepared by cathodic reduction. Solutions obtained in this way have been examined spectrophotometrically in order to measure the pK of phenyl-hydroxylamine and to study the acid catalysed re-arrangement to p-aminophenol.

(This work has been published in the Transations of the Faraday Society, and a reprint is included in the Appendix).

The half-wave potentials of several series of polycyclic aromatic hydrocarbons have been measured in ethylene glycol mono-methyl ether. These potentials are shown in the third part to be directly related to the wave-numbers of the p-bands in the absorption spectra of the hydrocarbons. Thus energy quantities derived from two very different measurement techniques are shown to be similarly related to molecular electronic distribution.

(A paper describing this work has been accepted for publication by the Faraday Society.)

I N D E X.

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Chemistry depends almost entirely on the behaviour of electrons. The full utilisation of the possibilities of the electron as a reagent has, however, been neglected until recently.

The study of the effects of electric currents on chemical compounds dates back almost to the development of the voltaic cell at the end of the 18th century. In 1800 Nicholson and Carlisle succeeded in the electrolysis of water using a voltaic pile. The use of the electric current as a chemical agent was illustrated by Davy, who isolated sodium and potassium metals by electrolysis of their molten hydroxides. In 1833 Faraday showed that there was a direct relationship between the amount of electricity passed during an electrolysis and the amounts (in equivalents) of the substances evolved at each electrode. Faraday realised the possibilities of the electrical current as a synthetic agent through the medium of the "nascent" gases produced at the electrodes[1]. This work was not only a substantial advance in placing the phenomenon of electrolysis on a quantitative basis, but was also to be of far reaching significance in the development of methods of physico-chemical investigation. Daniell (ca. 1840) carried out some experiments on the mechanisms of electrode processes. By use of a porous diaphragm to separate anode and cathode solutions he showed

that anions and cations did not necessarily move to the same extent. Kolbe (ca. 1850) noticed the great reducing and especially oxidising power of electrodes on many of the substances he studied. When he attempted to oxidise carboxylic acids electrolytically, he obtained carbon dioxide, and substances he considered to be radicals. In the electrolysis of solutions of acetates and valerates he obtained 'methyl' and 'valeryl' at the anode; substances which were later shown to be ethane, and an iso-octane. This discovery initiated a spate of investigations of anodic oxidations.

During the latter half of the 19th century, there was a vigorous development of physical chemistry; i.e., the measurement and correlation of physico-chemical quantities in order to throw light on equilibria and reaction processes. Hittorf (ca. 1850) investigated the movement of ions under the influence of electric fields, and measured transport numbers. Kohlrausch studied the conductivity of many electrolyte solutions in the 1870s. Clausius (ca. 1860), Arrhenius, and Ostwald (ca. 1890) developed the theory of electrolytic dissociation considerably. Le Blanc (1893)[2] measured the "decomposition potentials" of a number of electrolytic solutions. To throw light on the discharge of ions he developed an apparatus for measuring the polarisation potentials at both cathode and anode with respect to a non-

polarised reference electrode[3]. Electrochemical theory and practice were making rapid progress; and in such an environment it was not surprising that the study of cathodic reduction should receive new impetus. The investigations of Elbs, Gatterman, Haber, Löb and Tafel added much to our knowledge of reduction processes. In his study of the electrolytic reduction of nitrobenzene (1898), Haber showed the essential features of the reactions; and distinguished between products of direct reduction, and those which resulted from secondary chemical changes such as rearrangements and condensations. In the description of this classical work[4], he states:- "The electric current has, up to now, been regarded as a reagent in organic electrochemistry, whose effects are determined by current density, duration of electrolysis, and occasionally by electrode materials. This is an imperfect view. Oxidation and reduction processes depend primarily on the potential of the electrode at which they occur, and current density, duration, and electrode material are significant only inasmuch as they determine the electrode potential and its variations during the electrolysis." In this analysis, Haber neglected the possible catalytic influence of electrode surfaces on the various processes associated with the electron transfer (or flow of current). Surface catalysis apart, however, the above criticism could

be applied until recently. Many reports of the electrolytic reduction of organic compounds forty years after Haber's statement placed great emphasis on electrode materials, current densities and duration, to the neglect of electrode potential control and measurement. Lingane[5], in 1945, pointed out the infrequent appreciation and application of the principles advocated by Haber. He gave as example[6] the neglect in the analytical and electrochemical literature of the well proved controlled potential technique of Sand (1906)[7] for the electrogravimetric determination of metals.

The value of a cathodic reduction will be best utilised when the "reduction potential" of the depolariser is known. The study of electromotive force was inevitably connected with early electrochemical work, for the action of the cells used to produce voltage was erratic and imperfectly understood. With the production of cells with reproducible properties such as those of Daniell, Clark and Weston, the picture became clearer. The development of thermodynamics in the 19th century led to its application to the study of cell potentials, and the potentials of individual electrodes. A general thermodynamic theory of concentration cells was developed by Helmholtz. A study of the thermodynamics of electrodes consisting of a metal in contact with a solution of its ions led Nernst to postulate his "solution pressure" theory (1889)[8].

This theory received support from the demonstration by Le Blanc of the reversibility of the hydrogen electrode (1893). The first attempts at measuring oxidation reduction potentials were made by Bancroft (1892)[9]. The potentials obtained by him at a platinum electrode dipping into solutions of various reducing and oxidising agents gave approximate values of the right order. In many cases, however, his results had little fundamental significance because the oxidation-reduction processes involved were irreversible, and because of the lack of control over the relative concentrations of reduced and oxidised forms. Later investigations of reversible systems also met with difficulties. In many cases it was difficult to measure the concentration or activity of the reduced or oxidised forms. Additional complications were caused by variation in electrode properties owing to changes in the electrode surface. Most organic compounds are, however, reduced irreversibly, and the potential of an electrode in contact with a solution of a compound, while giving some indication of the reducibility, is not a reproducible or fundamental quantity. In addition, such measurements are often complicated by polarisation of the electrode. It is not easy to estimate the contribution made to electrode polarisation by deposition of a gas film, or a metal, by attack of the electrode metal, or otherwise

modification of the electrode surface. Concentration polarisation, due to depletion or enrichment of the solution in the neighbourhood of the electrode with respect to the active substance will often provide information about reduction processes.

Polarography.

The discovery of the dropping mercury electrode by Heyrovsky[10] in 1922 laid the foundation for the technique of polarography, which has added a vast amount of information about chemical structure, kinetics, reaction mechanisms to our knowledge. The particular advantage of the dropping mercury electrode is that its surface is being constantly renewed giving good reproducibility of results. The reduction of many metals was studied by Heyrovsky and his school by plotting current/voltage curves; at first by applying potential increments manually, then with the polarograph[11], an instrument which applied a continuously increasing potential, and automatically recorded the corresponding current. Curves, similar to the decomposition curves of Le Blanc, were obtained. Unless the concentration of the reducible material was unusually large, however, the curve flattened off owing to concentration polarisation; the final result being a so-called S-shaped curve.

The polarographic method was used to investigate the

reduction of many compounds in the schools of Heyrovsky, Shikata, and Semerano[12]. The height of the S-shaped polarographic wave was, in most cases, found to be proportional to the concentration of the reducible substance. This relationship was studied by Ilkovic[13]. He assumed the rate of diffusion of the reducible species across the diffusion layer to be directly proportional to the difference in concentration between the surface layer (C^o), and the bulk of the solution (C). The current i is in turn controlled by the rate of diffusion of the substance (in presence of a sufficient concentration of the supporting electrolyte).

$$\therefore \qquad i = K (C - C^o) \qquad \text{---------- (1)}$$

When the diffusion plateau is reached, i.e., $i = i_d$, concentration polarisation is almost complete, and C^o will become very small compared with C. Hence

$$i_d = K C \qquad \text{---------- (2)}$$

where K is the diffusion current constant. From theoretical considerations, Ilkovic[13] showed this constant to be a function of the number of electrons used in the reduction n, the diffusion coefficient of the reducible species D, the rate of flow of mercury m, and the drop time t. The characteristic Ilkovic equation,

$$i_d = 607\ n\ D^{1/2}\ C\ m^{2/3}\ t^{1/6} \qquad \text{---------- (3)}$$

was found to be obeyed, within experimental error, for the

reduction of almost all the substances studied. This equation has since been modified[14], but the corrections applied are, in most cases, small enough to be neglected.

Lack of appreciation of the theoretical significance of the rising part of the polarographic wave delayed the derivation of potential values truly characteristic of the compounds studied. Heyrovsky's original "tangent potential" was obtained from the point of contact of the wave as obtained in his polarograph, and a 45° tangent. Semerano used the point of contact of a tangent of slope $35^{\circ}16'$, the point of maximum curvature. Shikata noted that value of e.m.f. at which an increase of 10 mV resulted in a current increase of 1.9×10^{-8} amps. All these methods suffer from the defect that they result in a value which is dependent on C, m, and t. Furthermore, the first two methods are applicable to only one galvanometer sensitivity.

In 1935, Heyrovsky and Ilkovic derived the technique of "half-wave potential" measurement[15]. They showed this quantity, henceforth referred to as $E_{\frac{1}{2}}$, to be characteristic of the reduced compound, and in the case of reversible reductions to be closely related to thermodynamic quantities. A summary of their proof, and its applicability to various processes, follows.

Let us consider a reversible reduction of the form:

$$Ox. + ne \rightleftharpoons Red.$$

It follows from equations (1) and (2) that,

$$C^{\circ}_{Ox} = C_{Ox} - i/K_{Ox} = (i_d - i)/K_{Ox} \quad \text{----- (4)}$$

If no reduced species is present originally,

$$C^{\circ}_{Red} = i/K_{Red}$$

where K_{Red} is of the same form as K_{Ox}, being, however, a function of the diffusion of Red. into the solution.

$$\text{Now } E = E^{\circ} - \frac{RT}{nF} \ln \frac{C^{\circ}_{Red} f_{Red}}{C^{\circ}_{Ox} f_{Ox}} \quad \text{-------- (5)}$$

where C° represents concentration at the electrode surface, and f activity coefficient.

Substituting for C°_{Red} and C°_{Ox}

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{i \quad K_{Ox}}{K_{Red}(id-i)} \cdot \frac{f_{Red}}{f_{Ox}}$$

$$\text{i.e., } E = E^{\circ} - \frac{RT}{nF} \ln \frac{i}{(id-i)} - \frac{RT}{nF} \ln \frac{f_{Red} K_{Ox}}{f_{Ox} K_{Red}} \quad \text{---- (6)}$$

At the half wave potential, $E = E_{\frac{1}{2}}$, and $i = i_d/2$.

$$E_{\frac{1}{2}} = E^{\circ} - \frac{RT}{nF} \ln \frac{f_{Red} K_{Ox}}{f_{Ox} K_{Red}} \quad \text{---------- (7)}$$

$$\therefore E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{i}{(i_d-i)} \quad \text{---------- (8)}$$

This is the basic equation for the polarographic wave, first derived by Heyrovsky and Ilkovic[15].

Now K_{Ox} and K_{Red} depend similarly on the characteristics of the electrode, so K_{Ox}/K_{Red} can be effectively put equal to $\sqrt{D_{Ox}/D_{Red}}$ which is constant for a particular medium

at a given temperature. Similarly, f_{Red}/f_{Ox} can be expected to be constant for the particular species concerned. From equation (7), therefore, $E_{\frac{1}{2}} = E^{o}$ - const. i.e., $E_{\frac{1}{2}}$ is characteristic of Ox. and Red., and independent of concentration and electrode characteristics.

In most cases, the diffusion constants of the oxidised and reduced forms will not differ to any great extent, similarly for the activity coefficients, and $\frac{f_{Red} K_{Ox}}{f_{Ox} K_{Red}} = 1$. (Where $K_{Ox}/K_{Red} > 1$, and $f_{Red}/f_{Ox} < 1$, these differences may cancel out, and $(f_{Red} K_{Ox})/(f_{Ox} K_{Red}) \simeq 1$.) $E_{\frac{1}{2}}$ will then be equal to the standard potential E^{o} of the electrode Red., Ox.

In the case of the reduction of a metal ion to an amalgam of the metal,

$$M^{n+} + ne \longrightarrow M_{Hg}$$

the reduced form will be removed from the electrode surface not by diffusion into the solution, but rather by diffusion into the body of the mercury drop. Where the quantity

$$\frac{f_{Red}\ (\text{amalgam}).\ K_{Ox}\ (\text{solution})}{f_{Ox}\ (\text{solution}).\ K_{Red}\ (\text{amalgam})}$$

and the activity of the mercury are assumed unity, $E_{\frac{1}{2}}$ will be equal to the standard potential of the cell, Red.(amalgam)/Ox.(solution).

The reversible reduction of organic compounds will usually involve hydrogen ion.

$$R + ne + nH^+ \rightleftharpoons RH_n$$

Then, neglecting activity coefficients,

$$E = E^o - \frac{RT}{nF} \ln \frac{C^o_{RH_n}}{C^o_R} + \frac{RT}{F} \ln C^o_{H^+} \quad \text{---------- (9)}$$

If the solution is well buffered, $C^o_{H^+}$ should be appreciably the same as $[H^+]$, the bulk value of hydrogen ion concentration, and

$$E = E^o - \frac{RT}{nF} \ln \frac{C^o_{RH_n}}{C^o_R} - 0.059 \text{ pH} \quad \text{---------- (10)}$$

$$= E^o - \frac{RT}{nF} \ln \frac{i}{(i_d - i)} - \frac{RT}{nF} \ln \frac{K_R}{K_{RH_n}} - 0.059 \text{ pH}$$

$$E_{\frac{1}{2}} = E^o - \frac{RT}{nF} \ln \frac{K_R}{K_{RH_n}} - 0.059 \text{ pH} \quad \text{---------- (11)}$$

Thus in well buffered solution $E_{\frac{1}{2}}$ will still be independent of concentration, and electrode characteristics, but will vary by 0.059V for every unit change in pH. At a particular pH, however, $E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{i}{(i_d - i)}$

For the reduction of benzoquinone and the oxidation of hydroquinone, Müller[16] found $E_{\frac{1}{2}}$ to be equal to the standard potential of the quinhydrone electrode.

Where the reversible electrode process is followed by the irreversible transformation of the initial product, it has been shown by Kolthoff and co-workers[17], that the polarographic wave still has the normal form, e.g.,

$$A + ne \rightleftharpoons B \longrightarrow C$$

The formation of C at the electrode surface from B will be proportional to C^o_B. In turn the current will depend on the

formation of C,

$$\therefore \quad i = K_c \, C_c^o$$

$$\therefore \quad i = \frac{K_c \, C_B^o}{\alpha} \qquad \text{---------- (12)}$$

where α is the rate constant of the transformation. Substituting for C_B^o and C_A^o in equation (5) and neglecting activity coefficients, we obtain,

$$E = E^o - \frac{RT}{nF} \ln \frac{i}{(i_d - i)} - \frac{RT}{nF} \ln \frac{K_A \alpha}{K_c}$$

$$E_{\frac{1}{2}} = E^o - \frac{RT}{nF} \ln \frac{K_A}{K_c} - \frac{RT}{nF} \ln \alpha$$

Even when $K_A = K_c$, $E_{\frac{1}{2}}$ will differ from the standard potential of the reduction by a function of the rate constant of the transformation. The equation of the wave will, however, still be identical with equation (8).

Heyrovsky[15] has suggested that most reductions of organic compounds proceed irreversibly through the secondary reduction by means of primarily deposited "nascent" hydrogen, e.g.,

$$nH^+ + ne \rightleftharpoons nH$$

$$nH + R \longrightarrow RH_n$$

$$\text{then } E = E^o - \frac{RT}{nF} \ln \frac{[H]^n}{[H^+]^n} \qquad \text{---------- (13)}$$

Now the current will depend on the rate of utilisation of H, $\therefore \; d(RH_n)/dt = i \simeq \beta [H]^n \; [R]$ where all concentrations are those at the electrode surface. Substituting for [H] in equation (13), we obtain,

$$E = E^{o} - \frac{RT}{nF} \ln \frac{i}{\beta [R] [H^{+}]^{n}}$$

∴ in well buffered solution,

$$E = E^{o} - \frac{RT}{nF} \ln \frac{i}{(i_d - i)} + \frac{RT}{nF} \ln\beta - 0.059 \text{ pH} \quad \text{---} \quad (14)$$

and once again, by putting $i = i_d/2$, and then $E = E_{\frac{1}{2}}$, we obtain

$$E = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{i}{(i_d - i)}$$

The following relation has been found to hold for many irreversible reductions[18]:

$$i = C^{o} e^{\gamma EF/RT}$$

which gives the normal equation for the polarographic wave with a constant γ in place of n. γ is often found to be much less than unity, even for reductions involving several electrons.

Van Rysselbergh[19] attempted to explain this constant by the assumption of a polymerisation-adsorption of a number of reducible species together with a smaller number of hydrogen ions. This supposedly reversible and potential determining step was followed by further, fast reduction to the final product. This theory gave an equation of the polarographic wave containing two arbitrary parameters which had, however, no proved significance.

The application of the Nernst equation is valid only for equilibrium processes. Polarographic reduction involves

a rate process, rather than an equilibrium. The error introduced by Heyrovsky's application of the Nernst equation to polarography will, however, be small in the majority of cases, owing to the small currents involved.

The theory of "absolute reaction rates"[20] has been of value in explaining some quite complex processes[21]. As in other treatments, there is assumed to be at least one reversible and potential determining step (e.g., slow electron transfer). From a consideration of the various rate processes involved, an equation can be derived which, in a limiting case, corresponds to the Heyrovsky-Ilkovic equation for a polarographic wave.

The especial value of the polarographic method appears to be that where a process involves several irreversible processes and one reversible process, it singles out and indicates the reversible stage.

Let us consider the factors which are essential for polarographic studies, and the effect which their variation will have on the results.

Supporting electrolyte.

As the polarographic measurement is one of current against electrode voltage, it will be desirable to keep the solution resistance low. To achieve this a "supporting", or "Indifferent" electrolyte is used. In addition, where the reducible species is an ion, the presence of a large excess

of indifferent electrolyte will ensure that the reduction is determined not by the rate of migration of the species in the applied field, but by its diffusion. The variation in concentration of supporting electrolyte commonly met, (0.05 to 1 M), and consequent variation in ionic strength may affect activity coefficients and diffusion constants considerably. $E_{\frac{1}{2}}$ values may vary accordingly.

pH and Buffers.

The hydrogen ion concentration at the electrode surface may determine $E_{\frac{1}{2}}$ in three ways. The reducible species may be formed from a non-reducible one by a process involving H^+; hydrogen ion may be concerned in the actual electrode process; and the reduced form may undergo reaction with H^+. A buffer will, therefore, play an essential part in most polarographic media. The buffer will, however, require not only to regulate the pH value of the solution, but also to maintain the dynamic pH at the electrode surface equal to this value. Despite the large diffusion coefficient of the hydrogen ion, a large buffer concentration is required[22]. Of equal importance is the rate at which the buffer is able to adjust its composition to keep pH values constant. As in the case of supporting electrolytes, once again large ionic strengths are involved. An additional complication which may lead to "specific buffer" effects is due to the fact that many buffers contain polybasic

acids which are good complexing agents. In the case of reversible reduction, complex formation with either the oxidised or reduced form may introduce a slow, potential determining step. The $E_{\frac{1}{2}}$-value will become more negative. With irreversible reductions (where the reduction voltage does not represent a minimum energy) the formation of a complex may have a catalytic effect; and the $E_{\frac{1}{2}}$-value will become more positive.

Mixed solvents.

Few organic compounds are soluble in aqueous media, especially of high ionic strength. Accordingly, mixed solvents such as water/alcohol, and water/dioxan, have been extensively used. Conditions in such media are, however, not fully understood even at the present time. The concentration of ethanol was found to have a marked influence on $E_{\frac{1}{2}}$ values of nitro compounds[23,24], but the cause of this effect may be attributed to a number of factors. The alcohol will affect activities, and modify the properties of buffers considerably. Moreover, the electromeric or colorimetric determination of pH in mixed solvents may introduce further uncertainty.

Adsorption effects.

With heterogeneous processes such as occur at the electrode surface, the presence of surface active materials is bound to have a profound effect. If either the reducible material or reduction product is considerably adsorbed at the

electrode surface, the consequent alteration in activity will be reflected in the $E_{\frac{1}{2}}$-value. Surface active compounds are often added to polarographic solutions to suppress "maxima". Some of these compounds are suddenly adsorbed or desorbed at a particular potential, resulting in a wave. Others actually prevent some reduction processes from occurring until the desorption potential is reached.

Catalytic effects.

Some substances, e.g., thiols, though not themselves polarographically reducible, will result in waves. These waves are not linearly dependent on concentration, and are due to the catalysis by the active material of hydrogen evolution.

Reference electrode.

In the description of the polarographic method up to this point, only the single electrode potential of the dropping mercury electrode has been considered. This potential must, however, be measured with respect to another, non-polarisable, electrode. A large mercury pool electrode may be used. In the presence of halide ions, and when used as anode, this electrode should be well poised owing to the formation of a minute amount of mercurous halide. It cannot, however, be assumed that the potential will be equal to that of a "calomel" electrode of similar halide concentration, as

organic solvents, complexing agents, etc., will have some effect. An external reference electrode has been used (usually the saturated calomel electrode) but the use of this will introduce a liquid junction potential which can be minimised, but not eliminated.

It will be seen from a consideration even of the simple processes treated theoretically above (Heyrovsky-Ilkovic equation and applications), that necessary variation in experimental conditions will introduce variables into $E_{\frac{1}{2}}$ measurement. Where an attempt is to be made to obtain a quantitative correlation of $E_{\frac{1}{2}}$-values of a number of related compounds with other physico-chemical quantities, the number of variables must be minimised.

In recent years the study of non-aqueous solvents has been applied to the polarographic field. Solvents have been sought which can dissolve a large number of compounds, which have a high decomposition potential, and which can themselves regulate acidity function.

The present work falls into three sections, separate, but related.

In the first section, the properties of glacial acetic acid as a convenient polarographic medium are studied. This medium has been used for the investigation of a number of nitro-compounds. The results have been related to the

electron distribution in their molecules.

In the second section, the technique of Lingane for coulometric reduction at controlled potential has been used to investigate reduction products and reduction mechanisms of some nitro compounds, mainly in aqueous media. Spectrophotometry has been used in the study of some of the reduction products.

The third section deals with the polarography of a large number of polycyclic aromatic hydrocarbons in methyl cellosolve. The relationships of the results to absorption spectra, which depend similarly on the electronic structure of the hydrocarbons, have been noted.

Part 1.

Polarography of some Nitro Compounds in Acetic Acid.

INTRODUCTION.

The study of the effects of substituents on the properties of organic compounds has aroused much interest since the investigation of trichloracetic acid by Dumas in 1839. Ostwald (1889) attempted a quantitative measurement of such effects by application of physico-chemical methods. He measured the dissociation constants of a large number of organic acids by conductimetric methods[25]. Flürscheim[26] suggested a "polar factor", which was interpreted by G.N. Lewis[27] in terms of electronic distribution, and given the name "inductive effect" by Ingold[28]. In conjugated systems another effect was noted. Flürscheim used the concept of "alternating affinities", Lapworth the concept of "alternate polarity"[29]. The theory of the "electromeric effect" of Lowry[30] was extended and amplified to the permanent "mesomeric effect" of Ingold[31]. Many investigations of such effects have been made, by study of both kinetic and equilibrium processes.

The first application of polarography to such problems was by Shikata and Tachi[32], who, on the basis of the investigation of a number of organic compounds in Shikata's school, put forward the electronegativity rule of reduction potentials; "organic compounds are more readily reduced as more electronegative groups are substituted in the same molecule". Winkel and Proske[33] related the reduction potentials

of a number of carbonyl compounds to their structure, absorption spectra, and Raman spectra. Both these investigations suffer from the defect that they represent measurements of tangent reduction potentials made in essentially unbuffered solution. Many such studies have been made in recent years; in buffered solutions, and utilising $E_{\frac{1}{2}}$ measurement. It will, however, be seen from the discussion of polarographic conditions in the general introduction, that differing measurement conditions will make it difficult for results obtained by different workers to be compared. Elving et al.[34] state that ideally, $E_{\frac{1}{2}}$ should be compared in a given medium, at the same pH, buffer concentration, and ionic strength. Zuman[35] in his list of polarographic data stresses also that most results have only relative significance, and for comparison purposes only values obtained under similar conditions should be chosen.

The present study of the polarographic properties of acetic acid was carried out partly because of the intrinsic interest of measurements in such a strongly acid environment, and partly because comparisons of relative ease of reduction can be made very conveniently in such media.

James[36] has shown that concentrated (96-99%) sulphuric acid can be used as a polarographic medium, the self-ionisation of the acid being so extensive that no supporting

electrolyte is required. Measurements in this solvent are, however, restricted by the low decomposition potential (-0.7 V) to substances with $E_{\frac{1}{2}}$-value less than about -0.4 V, and the residual current corrections to be applied are somewhat large. Moreover, the effect of substituents on $E_{\frac{1}{2}}$-values is in many cases masked by the protonation of the reducible group. For this reason the properties of acetic acid have now been investigated as a more convenient acidic polarographic medium with a considerably higher decomposition potential.

The first investigation of acetic acid as a polarographic medium was made by MacGillavry[37] who studied solutions of inorganic salts in the pure solvent. A more detailed study was made by Bachman and Astle[38], who obtained polarographic curves for a number of metal ions, benzil, benzoin, and quinhydrone, using ammonium acetate as supporting electrolyte. They found that for substances of $E_{\frac{1}{2}}$-value more negative than -0.3 V, satisfactory waves were obtained.

The compounds studied are mainly aromatic nitro compounds as the effect of substituents on the ease of reduction is here of particular interest. The nitro group is strongly electrophylic, and therefore the electron density within it, and its ease of electron capture, will reflect the inductive and tautomeric effects of substituent groups.

Nitrobenzene was the first organic compound to be investigated polarographically. Shikata[39] recorded tangent reduction potentials for nitrobenzene at different pH values. These studies were extended by his school to nitrophenols[40], dinitrobenzene and dinitrophenols[41], and nitroaniline[42]. In recent years several careful studies of nitrobenzene[43] and aromatic nitro compounds in aqueous buffers have been made in the school of Astle[44], by Pearson[45], and by Page, Smith and Waller[24]. Nitroalkanes have been studied by Petru[47], DeVries and Iwett[47], Miller, Arnold and Astle[48], and Stewart and Bonner[49]. The products of reduction of nitrobenzene according to the scheme of Haber have been studied by Stocesova[50] and by Smith and Waller[51].

EXPERIMENTAL

Materials

Cylinder nitrogen was found to be satisfactory for removing oxygen from glacial acetic acid solutions. The nitro compounds used in this work were purified samples kindly supplied by Dr. J.D.C. Brand of this University, or were prepared and purified by standard methods. A specimen of γ-nitrotropolone (m.p. 194°C) was kindly supplied by Dr. R.A. Raphael and Dr. D. Steel. A.R. acetic acid was purified and dried by Orton and Bradfield's method[53]; from the melting point of the purified sample (16.50°C) less than 0.05% water was present. Ammonium acetate was purified by recrystallising an A.R. sample from glacial acetic acid and drying in vacuo over KOH. Chloranil was B.D.H. material. Tetrachlorohydroquinone was obtained by reduction of chloranil, using phosphorous and hydriodic acid[54], and thrice recrystallised from glacial acetic acid. After being allowed to stand in air to lose the acetic acid of crystallisation, the material melted at 236-237°C.

Apparatus

Polarograph

A Tinsley pen-recording polarograph was used. The applied voltage was, however, reduced to half, according to the expanded scale technique described by Werthessen and

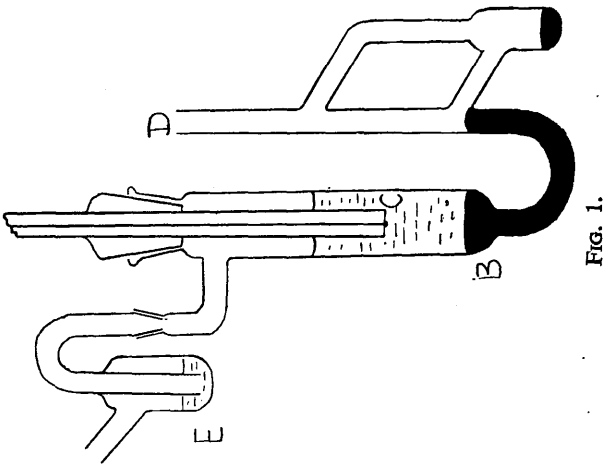


FIG. 1.

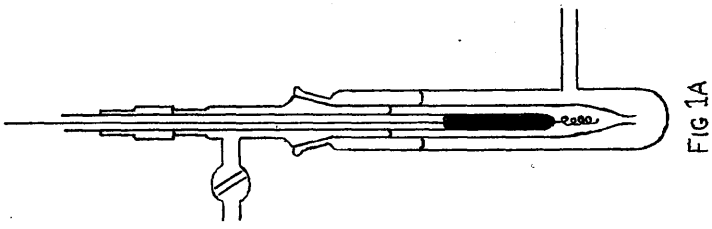


FIG 1A

figures 1 & 1A

Polarographic cell and chloranil electrode side-arm.

Baker[52]. This gave a rate of increase of voltage of 0.25V/min., and resulted in an improved accuracy of measurement owing to the twofold magnification of the voltage scale. The polarograph was calibrated before each measurement against a high resistance voltmeter, which had been in turn calibrated against a Marconi pH meter used as valve-voltmeter.

Cell

A polarographic cell of the type shown in fig.1 was used. The constant mercury level device maintained the mercury pool anode B at a fixed distance from the dropping mercury cathode C. The cell could be deoxygenated by bubbling nitrogen through D. The bubbler gas trap E prevented re-entry of oxygen into the cell. During the measurements the cell was kept in a thermostat maintained at a temperature of 25°C ± 0.05 C°.

Experimental Technique

Solution Resistance

Correction was made for the "ir" voltage drop across the rather large solution resistance of the cell. The minimum resistance Rmin, of the cell just before separation of a drop, was measured by an a.c. bridge method at 1000c/sec and found to be about 3000 ohms. Ilkovic[55] has shown that the mean resistance Rav. used for the ir drop correction is given by Rav. = 4/3 Rmin. A check on this correction was

given by plotting uncorrected half-wave reduction potentials against corresponding currents, when, as Muller[56] has pointed out, the slope of the line gives the solution resistance. Agreement between the two methods was good.

Electrodes

Capillary drop time t and rate of flow of mercury m were determined on open circuit in a 1 M solution of ammonium acetate in acetic acid by the methods described by Kolthoff and Lingane[57]. Two capillaries were used, with the following characteristics at a mercury head of 70 cm:-

(A) m = 1.650 mg./sec. t = 2.4 secs.,

(B) m = 1.090 mg./sec. t = 3.95 secs.

The variation of the quantity $m^{2/3}t^{1/6}$ with potential was found to be small and was neglected.

The half wave reduction potentials reported are referred to the potential of the mercury pool anode. In exploratory measurements, potentials were measured against the saturated chloranil electrode in a cell provided with a side arm as shown (fig. 1A) using a manual polarograph and a Marconi pH meter as valve voltmeter. The electrode solution was prepared as follows[58]:- 0.8 gm. tetrachloro-hydroquinone and 0.6 gm. chloranil were added to each 100 cc. of 1 M ammonium acetate/acetic acid solution, warmed to 50°C for $\frac{1}{2}$ min., then cooled to 25°C. A fresh solution was used every

day. Throughout these measurements the potential of the mercury pool anode remained consistently 0.035 V positive with respect to the chloranil electrode. This electrode has been shown to be a satisfactory reference electrode in acetic acid by Conant et al[59] and so for convenience, the mercury pool anode was used as reference electrode in subsequent work.

RESULTS.

Acetic Acid as Polarographic Solvent.

(1) Supporting electrolyte.

Bachman & Astle[38] found that the concentration of ammonium acetate should be above 0.25 M for minimum sensitivity of diffusion currents to change in electrolyte concentration. A concentration of 1 M was used in the present work to minimise the solution resistance. Decrease in ammonium acetate concentration was found to result in a slight displacement of reduction waves to more negative potentials as well as a tendency to increase the wave height. Neither of these effects, however, was at all critical.

(2) Water.

The effect of small changes in water concentration was investigated by stepwise addition of up to 1% water to the polarographic solvent. The solvent resistance (and hence

"ir drop" correction) was found to be markedly lowered; the $E_{\frac{1}{2}}$ values obtained were, however, not affected by such additions, provided correct allowance had been made for ir drop. Similarly A.R. acetic acid was found to be a satisfactory medium, in agreement with the results of Bachman and Astle[38].

(3) Oxygen.

MacGillavry[37] has stated that "ordinary precautions to exclude oxygen from the solution were quite superfluous" for polarography in acetic acid. For solutions of ammonium acetate in acetic acid, however, our measurements confirmed Bachman and Astle's[38] observation that polarographic reduction of oxygen occurred. Two waves were formed, the polarogram (fig 2) resembling that obtained with an aqueous solution of oxygen[60]. The second wave coincided with a wave obtained from an air-free solution of hydrogen peroxide (as is also the case in aqueous media[60]) and it appears probable that reduction, both in acetic acid and in aqueous solution, occurs by the same mechanism

$$O_2 + 2H^+ + 2e \longrightarrow H_2O_2 \quad \text{(first wave)},$$

$$H_2O_2 + 2H^+ + 2e \longrightarrow 2H_2O \quad \text{(second wave)}.$$

For the present work, dissolved oxygen was removed by bubbling a stream of nitrogen through the solutions for 30 mins.; the residual current was then less than 0.4 mmA for applied

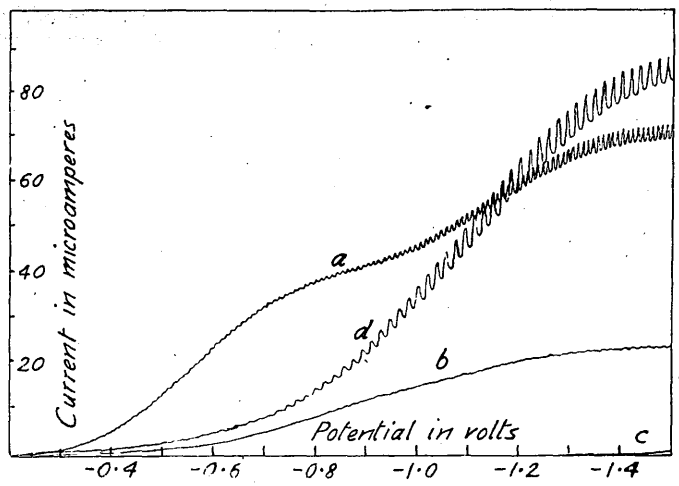


FIG. 2.—Polarograms for acetic acid + 1 M ammonium acetate;
(*a*) saturated with oxygen;
(*b*) saturated with air;
(*c*) air removed by passage of nitrogen for 30 min;
(*d*) + 3×10^{-2} M H_2O_2, deaerated with nitrogen.

potentials of up to -1.3V. The decomposition potential of the medium under such conditions was about -1.6V.

(4) Nitro compounds.

In general, nitro compounds in acetic acid gave well-defined and reproducible polarographic waves, the polarograms for nitrobenzene given in fig.3 being typical. Maxima occurred in some cases at concentrations above 2 mM, but were almost invariably suppressed by the addition of 0.01% gelatin. The effect of gelatin in suppressing the maximum which appeared in the p-nitrobenzoic acid wave is illustrated in fig.4. Tangents were drawn to the portions of the waves with minimum and maximum slope, and the diffusion current and half-wave potentials evaluated from the points of intersection of the tangents. Over the range 0.5 to 5 mM, diffusion currents were directly proportional to concentration, as required by the Ilkovic equation, and $E_{\frac{1}{2}}$ values constant, and independent of concentration. The results are given in Table 1. Each half-wave potential and diffusion current value reported is the mean of two consistent determinations, usually at concentrations of 2 and 5 mM, experimental error amounting to $\pm$2% for the diffusion currents, and $\pm$0.005 V for the half-wave potentials.

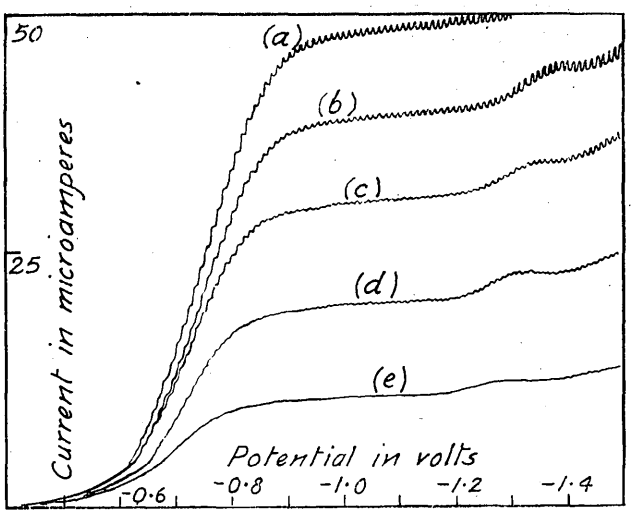


FIG. 3.—Effect of concentration on the reduction of nitrobenzene.
(*a*) $5{\cdot}0 \times 10^{-3}$M; (*b*) $4{\cdot}0 \times 10^{-3}$M; (*c*) $3{\cdot}0 \times 10^{-3}$M; (*d*) $2{\cdot}0 \times 10^{-3}$M; (*e*) $1{\cdot}0 \times 10^{-3}$M.

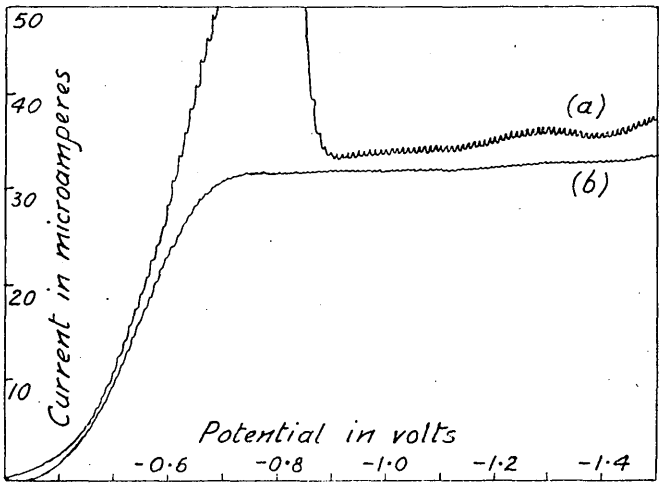


FIG. 4.—Effect of gelatin on the polarogram for *p*-nitrobenzoic acid: (*a*) no gelatin; (*b*) 0·01 % gelatin.

Table 1.

Polarographic Half-wave Potentials in Acetic Acid

Substance	$-E\frac{1}{2}$(V)	$i_d/cm^{2/3}t^{1/6}$
Nitrobenzene	0.675	5.95
m-dinitrobenzene	0.560	10.3
p-dinitrobenzene (a)	0.430	5.6
(b)	0.730	9.4
sym.-trinitrobenzene	0.450	13.4
m-fluoronitrobenzene	0.635	5.9
p-fluoronitrobenzene	0.705	5.9
o-chloronitrobenzene	0.645	5.6
m-chloronitrobenzene	0.580	5.6
p-chloronitrobenzene	0.615	5.3
o-bromonitrobenzene	0.620	5.4
m-bromonitrobenzene	0.550	5.2
p-bromonitrobenzene	0.575	5.3
m-iodonitrobenzene	0.515	5.1
p-iodonitrobenzene	0.535	5.1
3:5-dichloronitrobenzene	0.490	5.1
m-nitrobenzene sulphonic acid	0.595	3.3
p-nitrobenzene sulphonic acid	0.570	3.2
m-nitrobenzoic acid	0.575	4.1
p-nitrobenzoic acid	0.490	4.2
o-nitrotoluene	0.715	5.5

Table 1 (Contd.)

Substance	$-E_{\frac{1}{2}}$ (V)	$i_d/cm^{\frac{2}{3}}t^{\frac{1}{6}}$
m-nitrotoluene	0.635	5.4
p-nitrotoluene	0.665	5.6
4-nitro-o-xylene	0.670	5.1
o-nitrophenol	0.600	5.6
m-nitrophenol	0.605	4.1
p-nitrophenol	0.670	4.9
o-nitroaniline	0.735	7.4
m-nitroaniline	0.630	4.9
p-nitroaniline	0.740	6.4
m-dimethylamino-nitrobenzene	0.605	5.1
p-dimethylamino-nitrobenzene	0.720	7.1
m-nitroacetanilide	0.580	3.5
p-nitroacetanilide	0.625	3.7
∝-nitronaphthalene	0.565	4.9
ɣ-nitrotropolone	0.450	4.1
nitromethane	1.125	6.0
nitroethane	1.100	5.9
1-nitropropane	1.100	5.9
2-nitropropane	1.140	5.4
azoxybenzene	0.735	4.8
azobenzene (a)	0.250	2.0
(b)	0.70	1.1

Table 1 (Contd.)

Substance	$-E_{\frac{1}{2}}$ (V)	$i_d / cm^{\frac{2}{3}} t^{\frac{1}{6}}$
hydrazobenzene	not reduced	
p-aminophenol	not reduced	
nitrosobenzene (a)	0.13	2.4
*(b)	0.89	0.48
*(c)	1.20	0.42
N-phenylhydroxylamine (a)	0.70	0.33
*(b)	1.0	0.12

*poorly defined wave.

DISCUSSION.

For a reversible polarographic reduction, the plot of cathode potential against log $i/(i_d - i)$ should be linear, with slope $0.059/n$; where n is the number of electrons involved in the reaction. With the mono-nitro compounds studied in acetic acid, the slopes were about 0.06 for a representative number of compounds. As the overall reduction involves 4 or 6 electrons, and is irreversible, this may indicate the presence of an initial reversible process involving one electron.

Although $E_{\frac{1}{2}}$-values for irreversible reactions are rate constants rather than equilibrium constants, it is generally accepted that substitution theory can be applied to free energies of activation in much the same way as to thermodynamic free energies of reaction in the equilibrium case. For closely related series of compounds, such as the m- or p-substituted nitrobenzenes, it is probable that the difference between the $E_{\frac{1}{2}}$-values for two compounds is a measure of the difference in the potential energies of activation, and can be accounted for in terms of the known polar effects of the substituents. Thus Shikata and Tachi[32] put forward their electronegativity rule of reduction potentials. From the study of some nitro compounds, Astle[61] further concludes that where substitution causes the nitrogen to be left

more positive than in a normal nitro group, resonance within the group is decreased, and the nitro compound is more readily reduced. If the first step is the addition of an electron to the first unoccupied molecular orbital at a particular atom, then reduction should be facilitated by decrease in electron density at that atom. (Maccoll[62] has in fact shown that, with certain hydrocarbons, polarographic reduction proceeds at potentials determined by the energy of the first unoccupied molecular orbital.) In view of this, it is of interest to consider the reduction data for nitro compounds given in Table 1, and the effects of substituents on the relative ease of reduction given in Table 2. The inductive effect has been designated as I, and the tautomeric effect, being the sum of the permanent mesomeric effect, and the electromeric effect on the activated form, as T.

Polynitro compounds.

The introduction of further nitro groups into nitrobenzene facilitates reduction, as is to be expected from the strongly electron attractive (-I, -T) influence of the group. With p-dinitrobenzene two well-defined waves are formed, corresponding to stepwise reduction of the two nitro groups; whereas with m-dinitrobenzene and sym.-trinitrobenzene, composite waves correspond to the reduction of two and three nitro groups respectively.

Table 2.

The Effect of Substituents upon the Ease of Reduction of Nitrobenzene.

Substituent	Effect	Order of decreasing ease of reduction		Reference
		Acetic acid	Aqueous buffers	
-COOH	-I, -T	p- > m- > -H	p- > m- > o-	24
			p- > m- > o- > -H below pH 3 -H > p- > m- > o- above pH 3	61
$-CO.CH_3$	-I, -T	-	p- > m- > o-	61
$-NO_2$	-I, -T	p- > m- > -H	p- > o- > m-	61
			p- > o- > m- > -H	45
			o- > p- > m- > -H*	32
$-SO_3H$	-I, -T	p- > -m- > H	-	
-F	-I, +T	m- > -H > p-	-	
-Cl	-I, +T	m- > p- > -H	m- > p- > o- below pH 9 m- > o- > p- above pH 9	61
-Br	-I, +T	m- > p- > -H	-	
-I	-I, +T	m- > p- > -H	-	
$-O.CH_3$	-I, +T	-	m- > o- > p-	24

Table 2 (Contd.)

Substituent	Effect	Order of decreasing ease of reduction: Acetic acid	Order of decreasing ease of reduction: Aqueous buffers	Reference
-OH	-I, +T	o- ~ m- > -H ~ p-	o- ~ m- > -H ~ p- at low pH's -H > o- > m- > p- at high pH's	24
			o- ~ m- > -H > p- at low pH's m- > -H > o- > p- at high pH's	45
			o- ~ m- > -H > p-*	32
$-CH_3$	+I, +T	m- > p- ~ -H > o-	m- > p- > o- below pH7 m- > o- > p- above pH 7	61
$-NH_3^+$	-I	m- > -H > p- ~ o-	m- > -H > p- > o-*	32
$-N(CH_3)_2H^+$	-I	m- > -H > p-	-	
$-NH_2(OC.CH_3)^+$	-I	m- > p- > -H	-	

*Tangent potentials in 0.1 N HCl.

Nitrobenzoic and Nitrobenzenesulphonic Acids.

Both the -COOH and $-SO_3H$ groups exert a -I, -T influence, and deactivation should be greater at the o- and p-positions than at the m-position. This is in agreement with the observed orders of decreasing ease of reduction, p- > m- > H.

Halogeno-nitrobenzenes.

The order of decreasing ease of reduction (and hence of increasing electron density at the nitro group) is -I > -Br > -Cl > -H > -F for p-substitution and -I > -Br > -Cl > -F > H- for m-substitution. It is generally accepted that the inductive and tautomeric effects in halogeno-benzenes are opposed, the inductive effect (-I) being electron attracting in the order -F > -Cl > -Br > -I and the tautomeric effect (+T) being electron repelling in the same order. In the p-halogeno-nitrobenzenes the order is controlled by the tautomeric effect, and indicates an apparent increase in electron attraction from fluorine to iodine, the inductive effect being so far outweighed that the overall effect of fluorine as a substituent is that of electron release. (This is an inversion of the halogen order which prevails in, for example, the substituted acetic acids, where the inductive effect is the sole controlling factor.) Similar orders have been found for the overall chlorination rates for

halogen-benzenes, PhX, in aqueous acetic acid[63], and for the velocity constants for the hydrolysis of p-halogeno-benzyl chlorides in 50% aqueous acetone[64]. With the m-substituted halogeno-nitrobenzenes the contribution from the tautomeric effect is considerably smaller, presumably being relayed indirectly to the m-position. In consequence the overall electron attractive effect is greater with the m- than with the p-halogeno-nitrobenzenes, and the m-compounds are correspondingly more readily reduced; the difference being most marked with the m- and p-fluoronitrobenzenes.

Substitution of two halogen groups, as in 3:5-dichloro-nitrobenzene, gives the expected strong deactivation of the nitro group, the effect being twice that of a single m-chloro group.

Nitrophenols.

The -OH group exerts a -I and +T effect and, as with the halogeno-nitrobenzenes, the m- should be reduced more easily than the p-compound. In the case of the o-nitrophenol additional interaction may take place between the adjacent nitro and hydroxyl groups. It has been shown[44] (see Part 2) that the reduction products of o- and p-nitrophenols in aqueous media are somewhat anomalous, but the influence of substituents on the initial reduction step may be considered.

Nitroanilines and N-substituted Nitroanilines.

The nitroanilines are present in acetic acid as cations, and from the strong -I effect of substituents such as $-\overset{+}{N}HR_2$ it might be expected that reduction would be facilitated. In fact, o- and p-nitroanilines and p-N:N dimethyl nitroaniline are anomalous in that they are less easily reduced than nitrobenzene. In view of the fact that no mesomeric effect is possible with the protonated amino group, a steric effect must be postulated to explain this behaviour. The positive $-NH_3^+$ group will be strongly attracted by the cathode, and the molecule will orient itself with the negative nitro group away from the cathode surface; electron capture at the nitro group will thus be made more difficult by the presence of the polar ammonium group.

It has been shown (see p.56, Part 2) that p-nitroaniline is reduced in a 6-electron step, whereas m-nitroaniline is reduced in a 4-electron step, but this difference in reduction mechanism does not explain the above anomaly as pNN-dimethyl nitroaniline also gives a 4-electron reduction.

Nitrotoluenes and Nitroxylene.

Introduction of methyl groups into the p-, or both the m- and p-positions appears to have little effect on the $E_{\frac{1}{2}}$-values. o-Nitrotoluene is reduced less readily than nitrobenzene in agreement with the +I, +T effect of the methyl group. m-Nitrotoluene, however, is anomalous in being

reduced more readily than nitrobenzene.

Nitroalkanes.

Replacement of the electron-attracting phenyl group (-I, -T) by an electron repelling (+I, +M) alkyl group should lead to a marked decrease in ease of reduction. In agreement with this, the nitroalkanes studied were all reduced far less readily than nitrobenzene.

α-Nitronaphthalene.

Replacement of the phenyl group by the more strongly electron-attracting naphthyl group facilitates reduction.

γ-Nitrotropolone.

This compound is amphoteric, and is probably present as the ion $(NO_2.C_7H_6O_2)^+$ in acetic acid solution. The ease of reduction as compared to α-nitronaphthalene, nitrobenzene, and the nitroalkanes, gives an interesting indication of the aromatic nature of the tropolone ring.

Comparison of the present results with those of recent careful studies of nitro compound reduction in aqueous buffers[24, 43-45] is of interest. Astle and his co-workers[61] find the effect of substituents in facilitating reduction of aromatic nitro compounds to be in the order $-NO_2 > -COOH > -Cl > -CH_3$ in agreement with the results in acetic acid. Substituent effects in aqueous media in general and in acetic acid (Table 2) show a very marked similarity. Polarographic data for the

nitroalkanes in aqueous media[46-49] also indicate that, as in acetic acid, reduction occurs far less readily than with aromatic nitro compounds, while differences between the individual compounds are neither regular nor very marked. To summarise, if it be assumed that ease of reduction is facilitated by a decrease in electron density at the nitro group, then substituent effects, both in acetic acid and in aqueous media can, with very few exceptions, be accounted for by accepted views on the polar effects of the substituents.

In general, half-wave potentials in acetic acid appear to be closely related to the corresponding values in aqueous media, and the empirical equation

$$E_{\frac{1}{2}(HAc)} = E_{\frac{1}{2}(H_2O)} + 0.059\ pH - 0.40\ V$$

can be used to relate $E_{\frac{1}{2}(HAc)}$ the half-wave potential for a compound in 1 M ammonium acetate/acetic acid solution at 25°C to $E_{\frac{1}{2}(H_2O)}$, the corresponding value in an aqueous buffer of given pH. Agreement is usually to within 0.05 V. ($E_{\frac{1}{2}(HAc)}$ is measured against the mercury pool anode and $E_{\frac{1}{2}(H_2O)}$ against the saturated calomel electrode.)

Second Reduction Wave.

A second reduction wave, with $E_{\frac{1}{2}}$-value of about -1.2V, was observed with nitrobenzene (fig.3) and with most of the other aromatic nitro compounds studied in acetic acid. This wave was poorly defined, and in some cases was almost imperceptible or was absent (e.g., o-chloronitrobenzene and p-nitroaniline). In tabulating results, therefore, the half-wave potentials of these second waves have not been given. With nitrobenzene the diffusion current for the second wave was practically independent of the height of the mercury reservoir, indicating that it was probably kinetically controlled, and not diffusion controlled. Similar second waves have been observed in acidic aqueous buffers[24,45,50]. It appears to be accepted that, in aqueous media, four electron reduction of nitrobenzene to N-phenyl-hydroxylamine occurs in the first polarographic step. Stocesova[50] has shown that the second step is not diffusion controlled and suggests that a dimerisation reaction giving hydrazobenzene as a non-reducible product competes with the cathodic reduction of N-phenyl-hydroxylamine to aniline. Wawzonek[65] suggests that rearrangement of phenyl-hydroxylamine to p-aminophenol is the reaction competing with the cathodic reduction. A further investigation of the reduction mechanism is described in Part 2.

Related Compounds.

In addition to the nitro compounds described above, several related compounds which appeared to be of particular interest have also been investigated. Results are given in Table 1. The reducibility of azobenzene was decreased by the introduction of an NH_2 group at the para position, as in aqueous media[32] and in concentrated sulphuric acid[36]. Hydrazobenzene and p-amino-phenol gave no waves. With nitrosobenzene and n-phenyl-hydroxylamine, although the measurements were made on specimens prepared and purified immediately before use, the instability of these compounds and the ease with which traces of reducible decomposition products can be formed introduces some uncertainty into the results. Nitrosobenzene was reduced at a much lower applied potential than nitrobenzene, and this may account for the fact that the intermediate stage (nitrosobenzene reduction) in the Haber reduction mechanism is not observed in the polarogram for nitrobenzene.

$$-NO_2 \ (+ 2H^+ + 2e) \longrightarrow -NO \ (+ 2H^+ + 2e) \longrightarrow -NHOH.$$

Similar behaviour is found in aqueous buffers[51].

Part 2.

Reduction of some Nitro Compounds at a Stirred Mercury Surface.

INTRODUCTION.

The polarographic reduction of a series of closely related compounds will yield information about the influence of structure and substituents on ease of reduction, i.e., half-wave potentials. Information will also be obtained about reaction mechanisms, e.g., the number of waves observed, and their heights will indicate the number of separable stages, and the probable intermediates. In particular, the probable product of the stage represented by a particular polarographic wave can be deduced from n, the number of electrons involved. If the diffusion constant D of the reducible material is known, n may be calculated directly from the Ilkovic equation which is obeyed by the majority of polarographic processes.

$$Id = 607\ n\ D^{\frac{1}{2}}\ C\ m^{\frac{2}{3}}\ t^{\frac{1}{6}}$$

where Id is the diffusion current of the wave, C the concentration of the reducible material, m and t the easily measured capillary characteristics. Where D is not known in the reduction medium, as is often the case, one of two procedures is usually adopted. D, for the molecule in question, is assumed to be the same as that of an ion of similar size and structure, whose mobility can be measured in the medium, or of a molecule for which the reduction process, and therefore n, is known.

These procedures are likely to introduce errors, especially in mixed solvents, owing to differential solvation of molecules with different functional groups. Where n is large, as for instance in the reduction of picric acid, no definite conclusions may be reached as to the end product. Lingane[66] has sought to overcome this difficulty by direct measurement of the number of coulombs required to bring about complete reduction at a stirred mercury cathode under conditions of constant electrode potential. This involves the assumption, which in most cases is valid, that the processes occurring at the dropping mercury electrode and at a stirred mercury cathode are, if not identical, closely related. The electrolytic reduction of nitro compounds, despite the large bibliography, has not been extensively studied in this way. In the present work, the coulometric reduction of a number of aromatic nitro compounds (and related substances) has been investigated.

EXPERIMENTAL

Materials.

The mercury was purified by filtration, passage through a nitric acid column, washing with water, standing under concentrated sulphuric acid, washing again with water, drying and vacuum distillation. The acetic acid used as solvent

was purified, and the organic compounds studied were obtained as described in Part 1. The alcohol used was rectified spirits. The conc. sulphuric acid, and all other substances were of AnalaR grade. Cylinder nitrogen was found to be satisfactory for removing oxygen from the solutions used. The following buffer solutions were used:

(a) 0.1 M hydrochloric acid; pH ca. 1.

(b) 0.01 M hydrochloric acid, 0.09 M KCL; pH ca. 2.2.

(c) 0.1 M acetic acid, 0.1 M sodium acetate, 0.1 M NaCl; pH ca. 4.6.

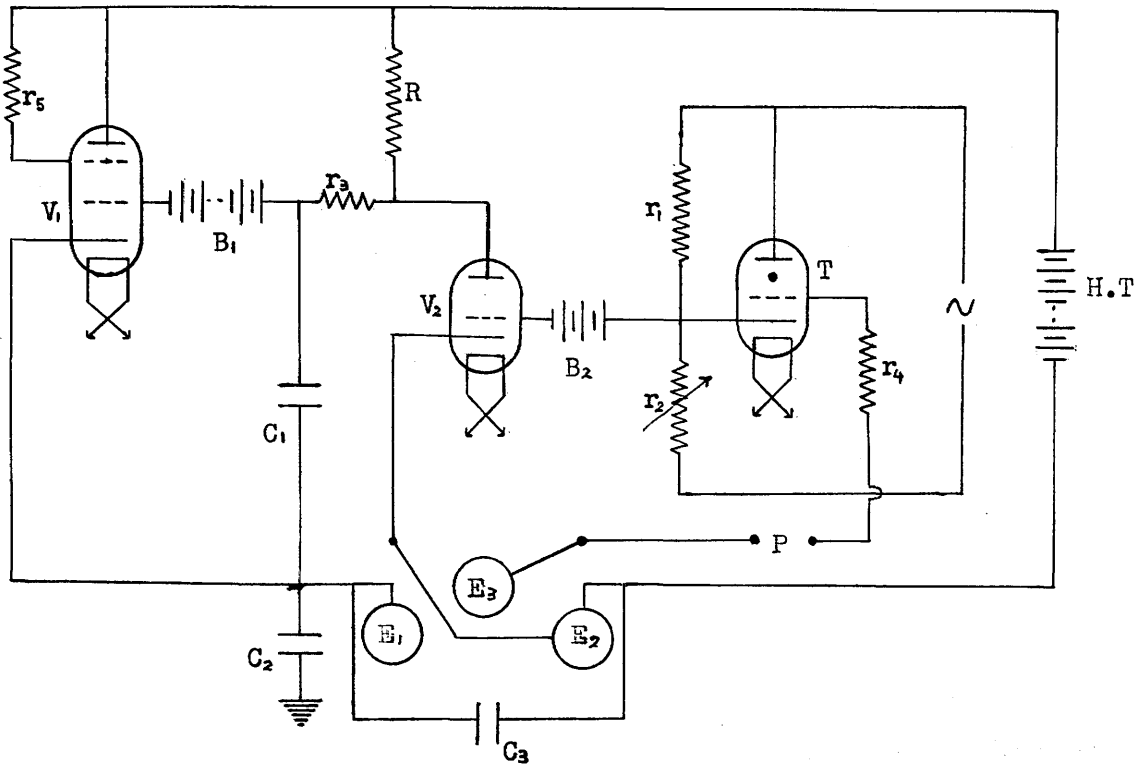
(d) 0.1 M borax, 0.1 M NaCl; pH ca. 9.2.

Apparatus.

Potentiostat

A number of methods for the automatic control of electrode potential has been described[67]. Lingane[68] developed an apparatus involving electronic relays and a motor driven rheostat. For convenience, however, the original all-electronic "potentiostat" of Hickling[69] was used in the present work. This apparatus was constructed with slight modifications (see Fig.5). The main control valve V_1 was a beam tetrode with a maximum current rating of 0.3 amps. The instability of the controlled potential was removed by (a) lowering the anode voltage of the thyratron T, (b) reducing the grid current of T by increasing the coupling resistor,

figure 5.



H.T.	250 V. D.C. from rotary converter.
A.C.	15 V. from mains transformer.
B_1	120 V. H.T. battery.
B_2	6 V. grid bias battery.
C_1	8μF electrolytic condenser.
C_2	16μF " "
C_3	2000μF " "
E_1	Cell anode.
E_2	Cell cathode.
E_3	Reference electrode.
P	Potentiometer.
R	5 Megohm resistor.
r_1	5 Kohm "
r_2	300 ohm rheostat.
r_3	100 Kohm resistor.
r_4	100 " "
r_5	250 ohm "
V_1	Mazda 12E1 beam tetrode.
V_2	Pentode CV1074 used as triode.
T	Thyratron GT1C.

(c) decoupling the cell anode line, and (d) damping the anode-cathode voltage oscillation with a large condenser. Provided the potentiostat had been allowed to warm up for at least ½ hr., the controlled potential, set by the potentiometer, did not change by more than 10 mV during a run. The potential of the stirred cathode was found to oscillate in phase with the stirrer, by at least 5 mV, so that more exact control was not warranted.

Reduction cell

The reduction cell was constructed from a 250 ml. flask, and is represented in the figure 6. The mercury pool cathode C was stirred by a magnetic float. To prevent re-oxidation of the reduction products, the anode was enclosed in the compartment B closed by a sintered glass disc; diffusion of solution through this proved to be negligible. The solution in the cell could be deoxygenated, and kept so by passing a stream of nitrogen through E.

Electrodes

A silver gauze spiral A, used as anode was completely satisfactory in aqueous media, provided that the chloride concentration was adequate (0.1 M), and that the silver chloride coating was prevented from becoming too thick by occasional cathodic polarisation in N sulphuric acid. In concentrated sulphuric acid an anode of lead wire was used, the coating of

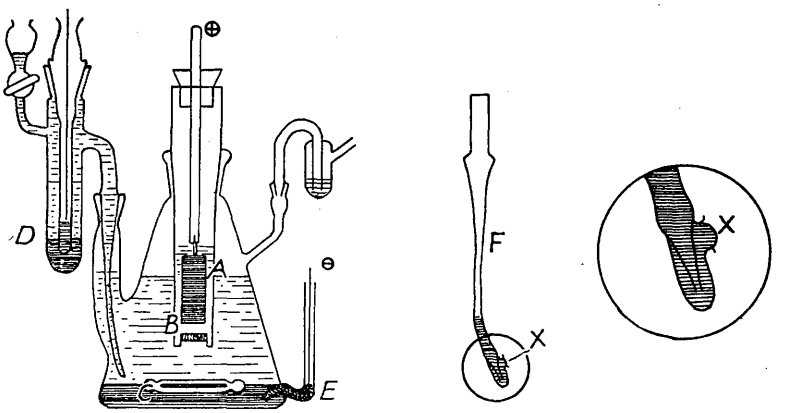


FIG. 6

(A) Silver gauze spiral anode.

(B) Anode compartment.

(C) Mercury pool cathode (with magnetic float stirrer).

(D) Calomel reference electrode.

(E) Nitrogen inlet.

(F) Reference electrode for non-aqueous media.

(X) Small mercury pool.

lead sulphate being removed mechanically after each determination. In glacial acetic acid a platinum cylinder anode was used. (Small bubbles of gas, probably ethane, were evolved from this electrode during electrolysis). The reference electrode D was a saturated calomel half-cell for aqueous media, with a saturated -KCl-agar salt bridge almost touching the surface of the cathode. For the other media, the calomel half-cell was removed and the electrode F substituted, the small mercury pool X acting as reference electrode.

Hydrogen-Oxygen Coulometer

Included in the main electrolytic circuit was a hydrogen oxygen coulometer of the type described by Lingane[66]. The gas compartment was constructed to hold about 150 cc., and a series of gas burettes or burette stems were prepared to hold the displaced liquid, of volume 100, 50, and 25 cc. according to the volume and accuracy required. The pressure tubing was purified by boiling in saturated caustic soda for 10 hrs., rinsing in water, boiling three times in N HCl for 2 hrs., rinsing thoroughly with water until the washings were neutral, then with distilled water. The electrodes were of platinum of area 1 sq.cm.

The coulometer was used as follows:- Prior to each determination the 0.5 M sodium sulphate solution used was saturated with the hydrogen-oxygen mixture by passing a

current of about 0.1 amp. for five minutes. During a run the liquid levels in the tube and burette were kept approximately equal in order to minimise error caused by change in the solubility of the gas with pressure. At the end of the determination the pressure of the gas was corrected for the vapour pressure of the solution at room temperature[66], and the volume of gas liberated converted to N.T.P. The coulometer had been found to liberate 0.1739 cc. of mixed gas per coulomb[66]. It was tested by using the potentiostat as a constant current device (applying a set voltage across a standard resistance in series with the circuit) and placing the gas coulometer in series with a silver coulometer. The quantity of electricity calculated from the gas coulometer agreed with that from the silver coulometer and with the current-time product to better than 0.5%.

Experimental Technique.

The normal procedure was as follows. The supporting electrolyte, consisting of a buffer solution at least 0.1 M in chloride and containing 0.01% gelatin, was added to the cell (100 ml.) and to the anode compartment (10 ml.) and it was de-oxygenated for 10 min. The potentiostat was set at a potential about 0.3 V more negative than that at which the reduction was to be carried out, and the solution was given a preliminary electrolysis to remove any reducible impurities.

This was continued until the current fell to a negligible value (ca. 1 mA). The electrolysis was interrupted, 10 ml. of concentrated alcoholic solution of the substance to be studied were pipetted into the cell, and nitrogen was bubbled again for 5 min. The potentiostat was then set at a value 0.1 V more negative than the half-wave potential of the reduction in question, the coulometer was put into the circuit, and the electrolysis started. It was continued until the current had once more fallen to a negligible value.

The apparatus was checked by using 50 mg. of copper in the form of its sulphate in a solution containing 0.4 M sodium tartrate, 0.1 M potassium hydrogen tartrate, and 0.3 M NaCl[66], the potential being maintained at -0.25 V. The value found for n was 2.02 electrons per molecule.

In concentrated sulphuric acid there was a high residual current. The coulometer reading was therefore plotted against time, and the amount of electricity corresponding to the reduction was estimated from the graph. With glacial acetic acid the residual current was small enough for the determination to be carried out in the ordinary way, at least for easily reducible substances.

RESULTS

The results are shown in the table. The potentials are negative, referred to the saturated calomel electrode in water, or to the mercury pool electrodes in the other solvents. E_r is the potential at which the reductions were carried out.

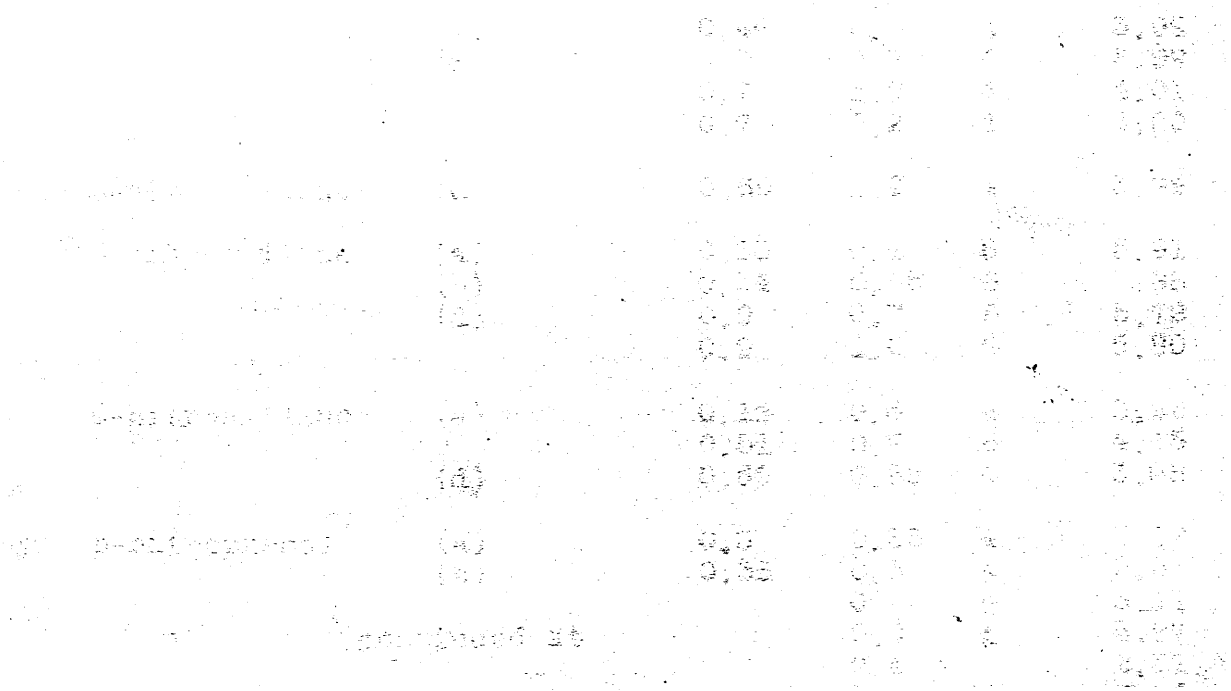


Table 3.

Substance	Solution	$E_{\frac{1}{2}}$ (volts)	E_r	Calc.	n_{Found}	Ref.
Nitrobenzene	(a)	0.2	0.35	4	3.92	45,24
	(a)	0.2	0.35	4	4.02	
	(a)	0.2	0.35	4	4.05	
	(a)	0.2	0.35	4	4.03	
continued after 1 h			0.9	6	6.16	
	(a)		0.9	6	5.86	
no gelatin			0.9	6	5.18	
			0.85	6	5.5	
			0.95	6	5.8	
	(b)	0.29	0.35	4	3.92	
		0.29	0.35	4	4.02	
			1.2	6	3.92	
	(c)	0.44	0.6	4	3.99	
	(d)	0.7	0.8	4	3.99	
		0.7	1.0	4	4.01	
		0.7	1.2	4	4.00	
p-nitrotoluene	(d)	0.69	1.0	4	3.99	45
p-nitroaniline	(a)	0.33	0.4	6	5.91	23
	(b)	0.54	0.65	6	5.88	
	(d)	0.9	0.7	6	5.72	
		0.9	1.0	6	5.80	
m-nitroaniline	(a)	0.12	0.3	4	3.96	35
		0.51	0.7	6	4.15	
	(d)	0.69	0.85	4	3.88	
p-nitrophenol	(a)	0.3	0.35	4	5.92	45,24
	(b)	0.36	0.5	4	2.5	
			0.6	4	3.11	
continued at			0.9	6	5.87	
			0.4		2.67	
	" "		0.7	4	3.06	
	" "		0.8		3.28	
	" "		1.0	6	5.38	
	(d)	0.87	0.9		5.99	
m-nitrophenol	(a)	0.25	0.35	4	4.19	45,24
	(d)	0.7	0.85	4	3.96	

Table 3 (Contd.)

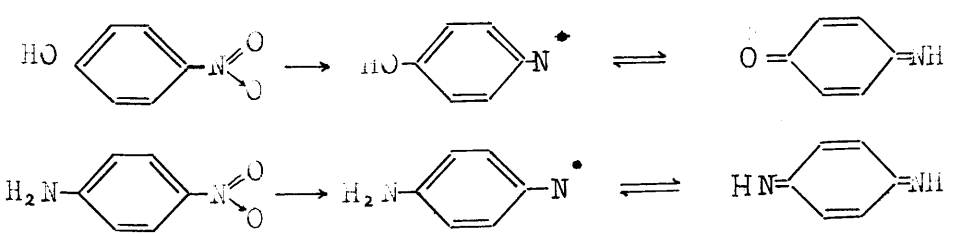
Substance	Solution	$E_{\frac{1}{2}}$ (volts)	E_r	Calc.	n Found	Ref.
p-dinitrobenzene	(a)	0.04	0.04	4	7.76	45
		0.23	0.75	12	13.06	
			0.00		10.4	
			0.00		10.55	
	(b)	0.23	0.35	4	11.2	
	(d)	0.34	0.45	4	1.92	
			0.5	4	6.16	
	continued at	0.80	0.9	8	9.19	
	" "		1.65	12	9.56	
m-dinitrobenzene	(a)	0.06	0.35	8	8.38	45
		0.18	0.35	8	8.5	
	(c)	0.27	0.65	8	8.39	
		0.33				
	(d)	0.46	0.55	4	1.31	
		0.68	0.8	8	7.62	
sym-trinitro-benzene	(a)	0.11	0.3	12	12.27	34
	(d)	0.65	0.8	12	11.9	
picric acid	(a)		0.65	12	16.7	45,68
			0.65	12	17.0	
			0.95	18	18.55	
			0.85		17.23	
			1.2	18	17.98	
p-nitroanisole	(a)	0.26	0.5	4	4.02	24
			0.5		3.94	
p-dimethylamino-nitrobenzene	(a)		0.5	4	4.4	
			0.5	4	4.03	
m-dimethylamino-nitrobenzene	(a)		0.5	4	4.72	
azobenzene	50% EtOH in					
	(a)	0.0	0.2	2	2.3	73
	(b)	0.3	0.5	2	2.24	
	(d)	0.57	0.75	2	2.3	
azoxybenzene	50% EtOH in					
	(a)	0.33	0.55	4	4.09	73
	(d)	0.9	1.1	4	3.89	

Table 3 (Contd.)

Substance	Solution	$E_{\frac{1}{2}}$ (volts)	E_r	Calc.	n_{Found}	Ref.
4-nitro-tropolone	30% EtOH in (a)	0.1	0.25		3.81	74
			0.5		4.36	
2-bromo-tropolone	(a)		0.95		3.68	
	(d)		0.8		2.51	
			1.5		2.93	
tropolone	(a)	0.96	0.95	1	0.865	75
	(c)	1.2	1.6	1	1.53	
	(d)	1.6	1.7	1	1.45	
	concentrated sulphuric acid					
nitrobenzene		0.25	0.2	4	3.79	36
m-bromonitro-benzene			0.2	4	4.21	
			0.2	4	4.26	
	glacial acetic acid					
p-nitrobenzoic acid		0.49	0.55	4	4.17	71
		0.49	0.55	4	4.11	

DISCUSSION.

In general the results for the electron-uptake agree with those that had been obtained using polarographic means. Thus, in a solution of nitrobenzene of pH 1, n is 4 for the first wave and 2 for the second. In less acid solutions the product of 4-electron reduction is apparently not further reducible under the conditions used, and n is 4. Polarographically, however, the second wave usually diminishes in height with increase in pH, but does not disappear until a pH of about 5 is reached[50]. For p-nitroaniline and p-nitrophenol n is 6, while both m-nitrophenol and m-nitroaniline give n = 4 for the first wave, indicating the probability of a difference in reduction mechanism[50]. When the p-hydroxy or p-amino group is fully methylated, as in p-nitroanisole and p-N:N-dimethyl nitroaniline, n is 4. This confirms the theory that the 6-electron reduction is due to the existence of an easily reducible p-quinonoid form of the p-substituted phenyl-hydroxylamine radical.



An intermediate of this form is impossible in the methylated compounds.

It appears from the reduction of poly-nitro compounds that reduction is often followed by condensation of the products in the well-stirred solution, thus complicating the mechanism. (Intense colours were produced in many cases.) This is in agreement with the data of Brand and Mahr[70] who found that the condensation between aryl nitroso and hydroxylamino groups was accelerated by the presence of m-nitro groups.

Azobenzene and azoxybenzene both appear to be reduced to hydrazobenzene with 2 and 4 electron reductions respectively. 4-Nitro-tropolone gave n = 4, probably representing the formation of a hydroxylamine. 2-Bromo-tropolone gave n = ca. 3, which probably represents reduction of the bromo group, followed by a reduction-condensation of the resulting tropolone. Tropolone itself appears to be reduced with n between 1 and 2; under the conditions used, there is probably competition between 1-electron reduction to a pinacol-like product, and complete reduction of a double bond.

In concentrated sulphuric, and in glacial acetic acid the nitro compounds chosen for their ease of reduction both gave n = 4 as expected.

SPECTROPHOTOMETRIC MEASUREMENTS

Part 2(a)

Rearrangement of Phenyl-hydroxylamine.

During the polarographic investigation of some nitro compounds in glacial acetic acid[71] (see Part 1, p.44), a second wave was observed in nearly all cases. The height of the wave was smaller than would correspond even to a one-electron reduction. The form of the wave did not suggest a catalytic wave. As no abrupt and large change in the double layer capacity was observed at the appropriate voltage in a similar solution[72] a desorption wave was ruled out. The wave therefore appeared to be due to some further reduction of the initial product; a reduction which had, however, to compete with an alternative reaction. This finds support in the observation that the wave height varied only to a very small extent with the height of the mercury column, indicating that the wave was not diffusion controlled.

In aqueous solutions of low pH a similar phenomenon had been observed and studied[50], and various competing reactions suggested[50,65]. Wawzonek has stated that the competing reaction must be the acid-catalyzed rearrangement of phenyl-hydroxylamine to p-aminophenol[65]. This theory was tested by the reduction of nitrobenzene to phenyl-hydroxylamine in buffer solutions, and a spectrophotometric comparison of the

resulting solutions with those of aniline and p-aminophenol. In acid solution, p-aminophenol was the only one to give a strong absorption peak (2725 Å). This peak was, however, not observed in any of the solutions of phenylhydroxylamine in 0.1 N HCl, even after several hours in an atmosphere of nitrogen. From these observations it seems unlikely that the acid-catalyzed rearrangement of phenyl-hydroxylamine in 0.1 N HCl in a well-stirred solution, is fast enough to compete with electrolytic reduction to aniline. In view of the observation of Haber[4] that phenyl-hydroxylamine is stable in acetic acid for several days, it is likely that the rearrangement to p-aminophenol plays only a small part in the polarographic mechanism in that solvent also.

Part 2(b)

pK-value of Phenyl-hydroxylamine.

There was a discrepancy between the pH-value at which phenyl-hydroxylamine is reducible (< 2.2), and that at which the polarographic wave disappears (ca.5)[24,45,50]. It therefore appeared desirable to measure the pK-value of phenyl-hydroxylamine. Electrolytic reduction in various buffers seemed the best method of preparation with the exclusion of oxygen. As the absorption spectrum of phenyl-hydroxylamine in neutral solution showed a distinct peak which was absent

in 0.1 N HCl, spectrophotometry appeared to offer a convenient method for measurement of its pK value.

When solutions of phenyl-hydroxylamine were examined in loosely stoppered cells, a fairly rapid rise in absorption was observed, presumably due to oxidation. When care was taken to exclude oxygen, e.g., by the use of stoppered cells, the rise in absorption became negligible.

A 0.0189M solution of nitrobenzene in rectified spirits was made up and 5 ml. used per determination. A variable buffer was made up containing: 0.05M phosphoric acid, 0.05M acetic acid, and 0.1M sodium chloride. By addition of 1M sodium hydroxide, buffers varying in pH from 2 to 6 were made up and 100 ml. used for each preparation. The reduction was carried out until the current fell to a value which indicated that all the nitrobenzene had been reduced, and the amount of electricity used corresponded to the use of 4 electrons per molecule. A siphon tube was substituted for the reference electrode in the reduction cell, and the solution blown over with nitrogen into the stoppered quartz cell. The absorption of the solution at 2760 Å was noted. The pH-value of a portion of the solution was determined with reference to a standard acetate buffer with a glass electrode. The spectra obtained are shown in Fig.7.

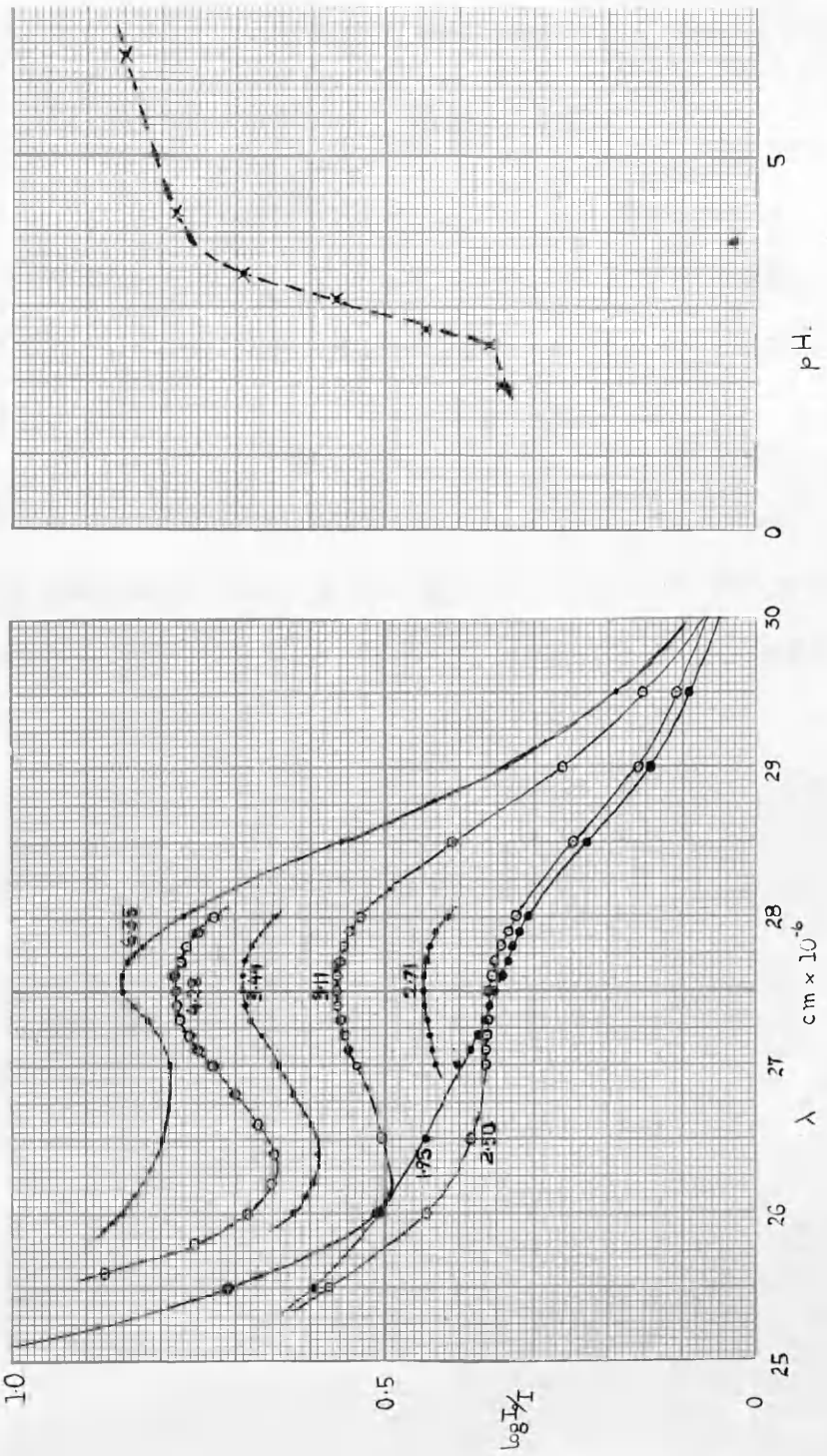


figure 7
Absorption spectra of Phenyl-hydroxylamine in acidic buffers.

The graph of absorption against pH had maximum slope in the region of pH 3. The phenyl-hydroxylamine was assumed to be completely unionised at pH 6.35, and half-ionised at pH 3. From this the fraction of unionised form present was calculated for each solution using the height of the absorption peak. The values for pH and log (Red)/(Ox) were substituted in the equation

$$pK = pH + \log \frac{(PhNHOH)}{(PhNHOH^{+})}$$

The average of the pK-values obtained was used in the re-calculation of (Red)/(Ox). By a number of such successive approximations the pK-value was calculated to be 3.2 ± 0.05.

Part 3.

The Polarography of Polynuclear Aromatic Hydrocarbons and the Relationship to their Absorption Spectra.

INTRODUCTION.

The growth of the dye-stuffs industry has had a profound effect on chemistry since the late 19th century. The three fields of cathodic reductions, colour theory, and aromatic hydrocarbons, played their part in the development of this industry, which in its turn provided a stimulus to further work in these fields.

Graebe and Liebermann[76] pointed out in 1868 that all the known organic coloured compounds lost their colour when they were reduced. Witt's Auxochrome theory[77] was the basis of many attempts to correlate colour and constitution. Owing to the complexity of most coloured compounds and the absence of any definite measure of colour or structural stability, these theories were, for a long time, qualitative in nature. The development of spectrophotometry enabled a more definite comparison of the colours of various compounds to be made, and gave an exact measure of their depth of colour. Stieglitz[78] regarded a dyestuff as being in a state of intermediate oxidation-reduction, as both oxidation and reduction generally tended to remove the colour. The colour was thus thought to be due to a form of intramolecular oxidation-reduction. As the qualitative resonance theory evolved into the study of quantum mechanics, colour and structural stability were slowly correlated to calculable

molecular energy levels.

The polynuclear aromatic hydrocarbons lend themselves very well to an investigation of variations in colour and reactivity. Owing to the fact that they are made up of only two elements, their molecules are reasonably homogeneous, and they exhibit a regular gradation of properties in their homologous series. This field owes a great deal to the work of Dr. E. Clar, who, in addition to synthesising most of the hydrocarbons known, has classified and related their spectra by a number of empirical rules, which enable the spectra of unknown hydrocarbons to be predicted.

Electrochemical measurements have provided a number of data in this field. The oxidation-reduction potentials of a number of quinones have been measured by Fieser and his collaborators[79] and correlated to spectra[93]. Laitinen and Wawzonek and their collaborators have studied the polarography of many conjugated compounds, using as solvent 75% dioxan containing tetrabutylammonium iodide as supporting electrolyte[80,81,82]. In particular, from the half-wave potentials of a number of polycyclic aromatic hydrocarbons[81,82], they sought to deduce the order of successive reductions at various sites in the molecule, and hence, their molecular structure. Maccoll[62] noticed the similarity between the mechanisms postulated for polarographic reduction and forma-

tion of alkali metal salts of such hydrocarbons. The latter process had been studied from a quantum-mechanical viewpoint by Hückel. Application of the zero-order molecular orbital calculations of Hückel to the hydrocarbons studied by Wawzonek et al. led to a linear relationship with $E_{\frac{1}{2}}$-values. This relationship was modified, but not appreciably affected, by Lyons[83], who introduced the solvation energy of the ionic reduction intermediate. Pullman, Pullman and Berthier[84] have studied this relationship using a first-order approximation M.O. method[85]. They pointed out that it was improbable that the data for different series of hydrocarbons should lie on the same curve. They also suggested that the $E_{\frac{1}{2}}$-values might bear some significant relationship to spectroscopic data, a relationship which was confirmed by Watson and Matsen[86]. They showed that, when the $E_{\frac{1}{2}}$-values obtained by Wawzonek et al.[80,81] were plotted against the wave-number of the absorption band in the spectrum of the hydrocarbons representing the first permitted electronic transition, a straight line resulted. Hoijtink and van Schooten[87] have discussed the wave-mechanical relationships, and have related the probable reduction products to the electron distribution in the ionic reduction intermediates.

A difficulty limiting the polarographic study of a

large range of polycyclic hydrocarbons arises from their low solubilities in useful solvents. The more soluble compounds of low molecular weight are difficult to reduce and require a solvent with high decomposition potential. Compounds with large molecules are usually more easily reduced, but are much less soluble. Glycol ethers have been used for the determination of naphthalene[88], and in the mono-methyl ether even pentacene is slightly soluble. This solvent has therefore been used in the present work, in which measurements have been made on over 70 compounds.

EXPERIMENTAL.

Materials

Ethylene glycol mono-methyl ether was purified by the method described by Parks and Hansen[88], the product distilling in the range 123-125°C. Tetrabutyl ammonium iodide was used as supporting electrolyte; after preparation and purification[80] it melted at 145-6°C. The hydrocarbons used were highly purified samples of synthetic or natural origin. Their formulae are represented in Figs.8 and 9 and individual compounds will generally be referred to by the Roman numerals appearing there. Many thanks are due to the following for the provision of these compounds: Miss M. Cameron, Dr. A.D. Campbell, Dr. N. Campbell, Dr. E. Clar,

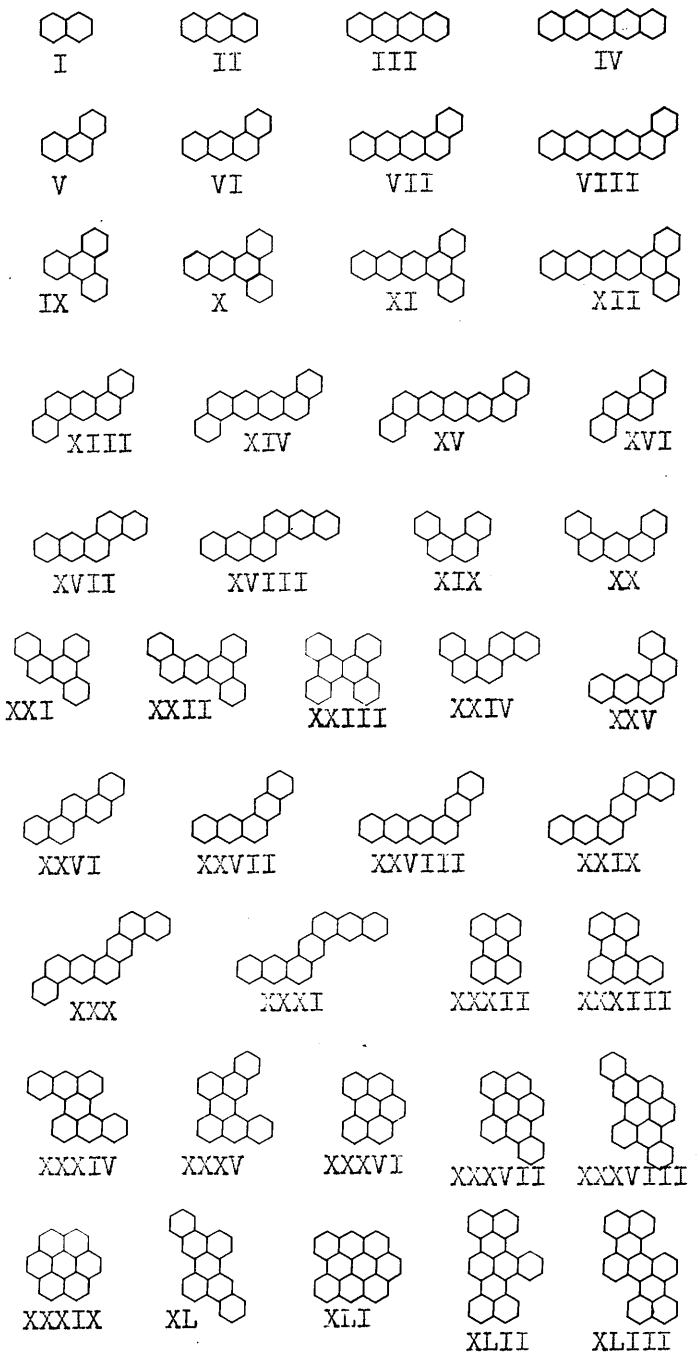

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figure 8

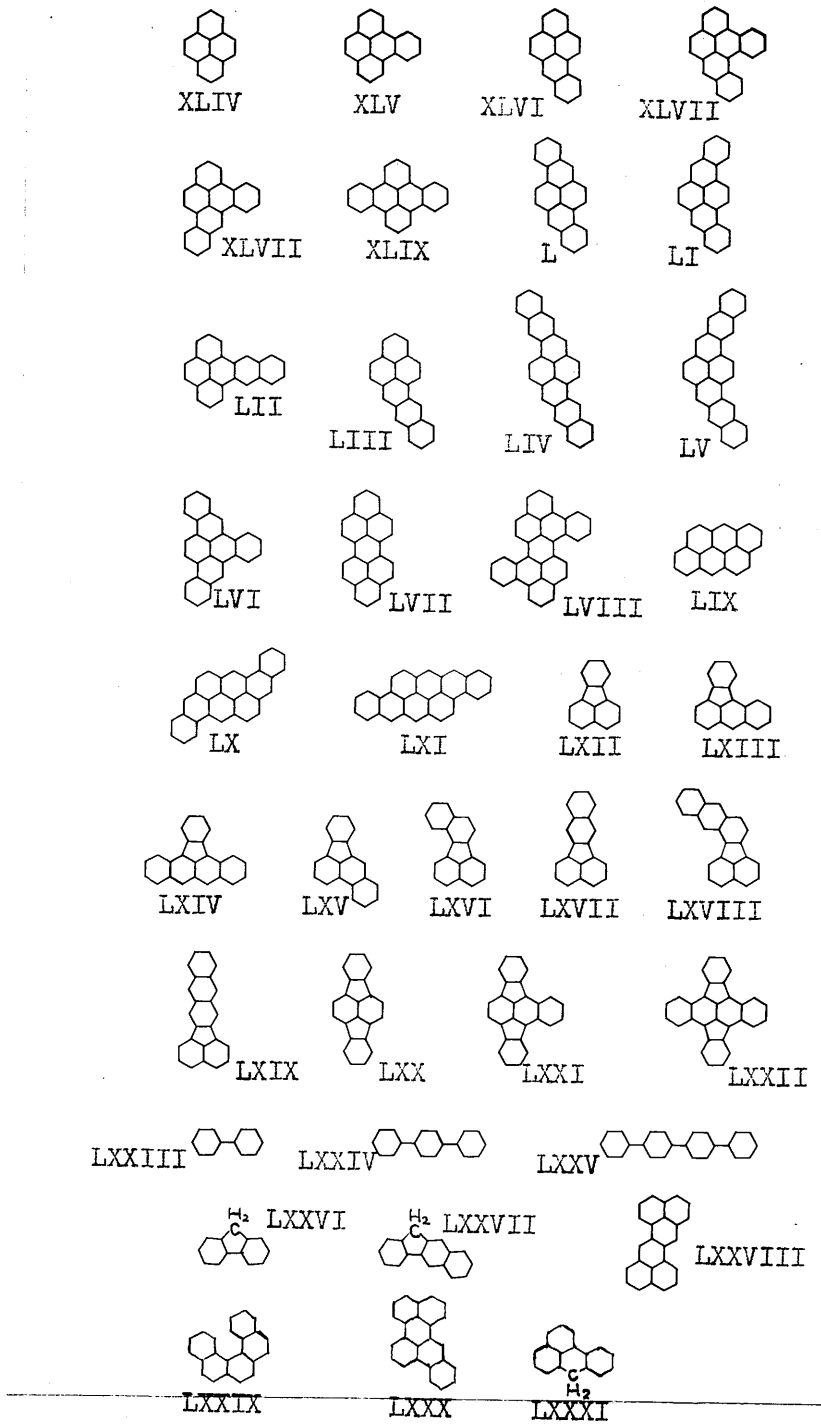
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figure 9

Professor J.W. Cook, F.R.S., Dr. C. Dufraisse, Mr. G. Kelly, Dr. C.L. Hewett, Dr. L. Reggel, Dr. Schoental and Dr. H.S. Tucker.

Polarographic Solution

Arthur and Lyons[89] found that anhydrous organic solvents gave spurious polarographic waves unless care was taken to de-oxygenate the solvent before bringing it into contact with mercury. Such precautions were even more important in the present work, because of the liability of sensitive compounds such as tetracene, to undergo photo-oxidation. Furthermore, when tetrabutyl ammonium iodide was dissolved in ethylene glycol mono-methyl ether in presence of air, a yellow solution often resulted, and despite subsequent de-oxygenation yielded polarograms showing a maximum at -0.1 V and erratic behaviour beyond -1.5 V. The yellow colour could indeed be removed by shaking the solution with mercury, but the unsatisfactory polarographic behaviour persisted. Even when the solution was prepared in the absence of oxygen, a small wave occurred at -0.12 V, and in some cases at -1.55 V. These difficulties could be largely overcome by pre-electrolysis of the solution in the cell described in Part 2 (Fig.6), using a silver anode and a stirred mercury cathode, the potential at the latter being held at -2.0 V until the current

fell to about 2 mA, and then at -3.0 V for a further 15 mins. The solvent containing 0.1 M tetrabutyl ammonium iodide, and pretreated in this way, was generally used in this work, and it may be referred to as solution A.

Apparatus and Experimental Technique.

To enable all operations to be carried out with rigorous exclusion of oxygen, the cell assembly illustrated in Fig.10 was adopted[90]. Cylinder nitrogen, after passing successively through solutions of alkaline hydrosulphite, with anthraquinone-β-sulphonic acid[91], of lead acetate, concentrated sulphuric acid, and finally through the polarographic solvent, was supplied at A. The hydrocarbon to be studied was first finely ground, and 0.5 to 3 mgm. of it were weighed into tube B; 10 ml. of solvent, previously deoxygenated, were pipetted in and the tube was covered with black paper. Nitrogen was then passed for ten minutes, the tube heated to ensure complete dissolution of the sample, and then cooled. The taps were so manipulated as to flush the cell out with nitrogen, and then to blow the solution over into the cell C. With certain compounds of very low true solubility, it was possible to use supersaturated solution. Even this device failed with compounds IV, XV, XVIII, XLI, LIV, LV, LX, LXI; but these solubilities could be sufficiently increased by adding 25% of thiophen-free

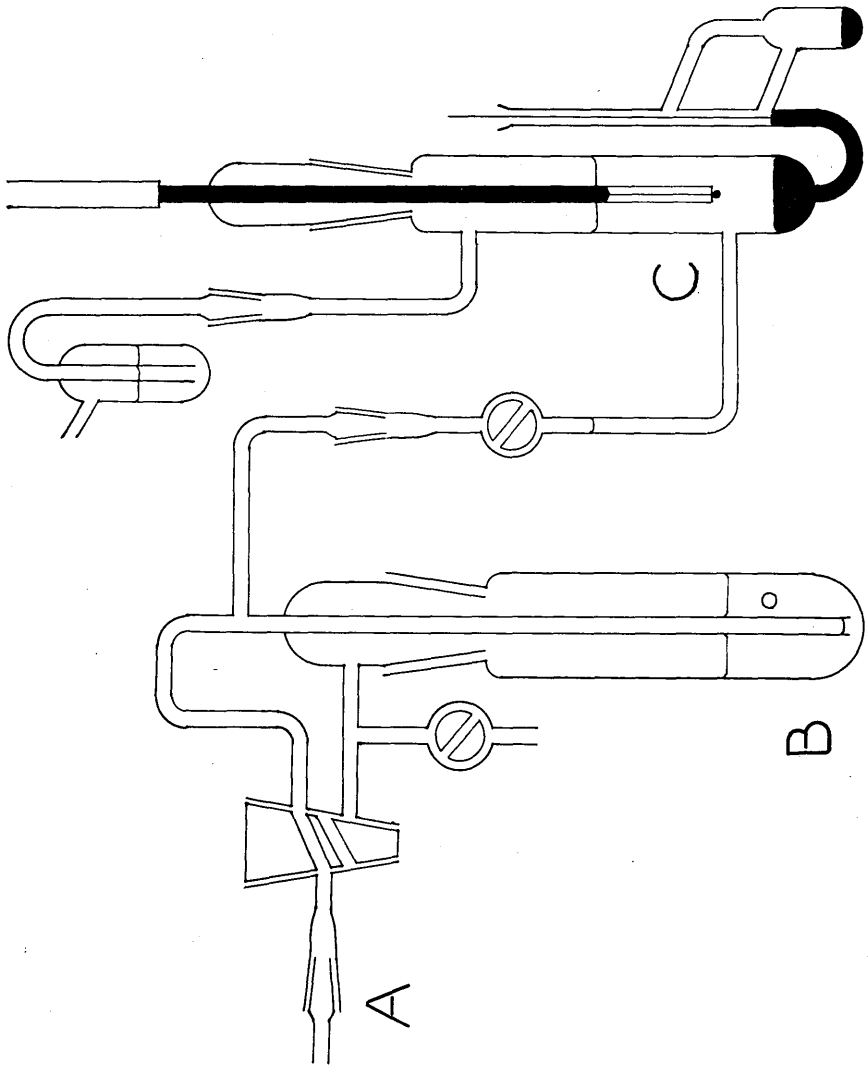


figure 10

Polarographic cell assembly.

benzene to the solvent (solution B). A direct comparison showed the mercury pool electrode to be 0.003 V more negative in solution B. Several compounds were investigated in both solutions A and B. The difference in $E_{\frac{1}{2}}$ (ca. 5 mV) was within experimental error.

Polarograms were recorded on a Tinsley instrument, with expanded scale[52], and a potentiometer in series. The minimum resistance R_{min}, of the cell was measured after each run, and the correction for the "iR drop" applied using 4/3 R_{min} as the average resistance[55]. R_{min} was about 3000 ohm for solution A, and about 4000 ohm for solution B. The dropping mercury electrode used had the following characteristics at a mercury head of 70 cm. on open circuit in the standard solution A: m = 1.174 mgm/sec., t = 3.18 secs. The variation of t with potential (see Fig.11) was examined by allowing the undamped polarograph to run at each potential, and measuring the distance recorded for 50 oscillations. All measurements were made at 25.0°C ± 0.1 C°. The decomposition potential of solution A was -2.15 V, but the decomposition was in some cases delayed by reduction processes.

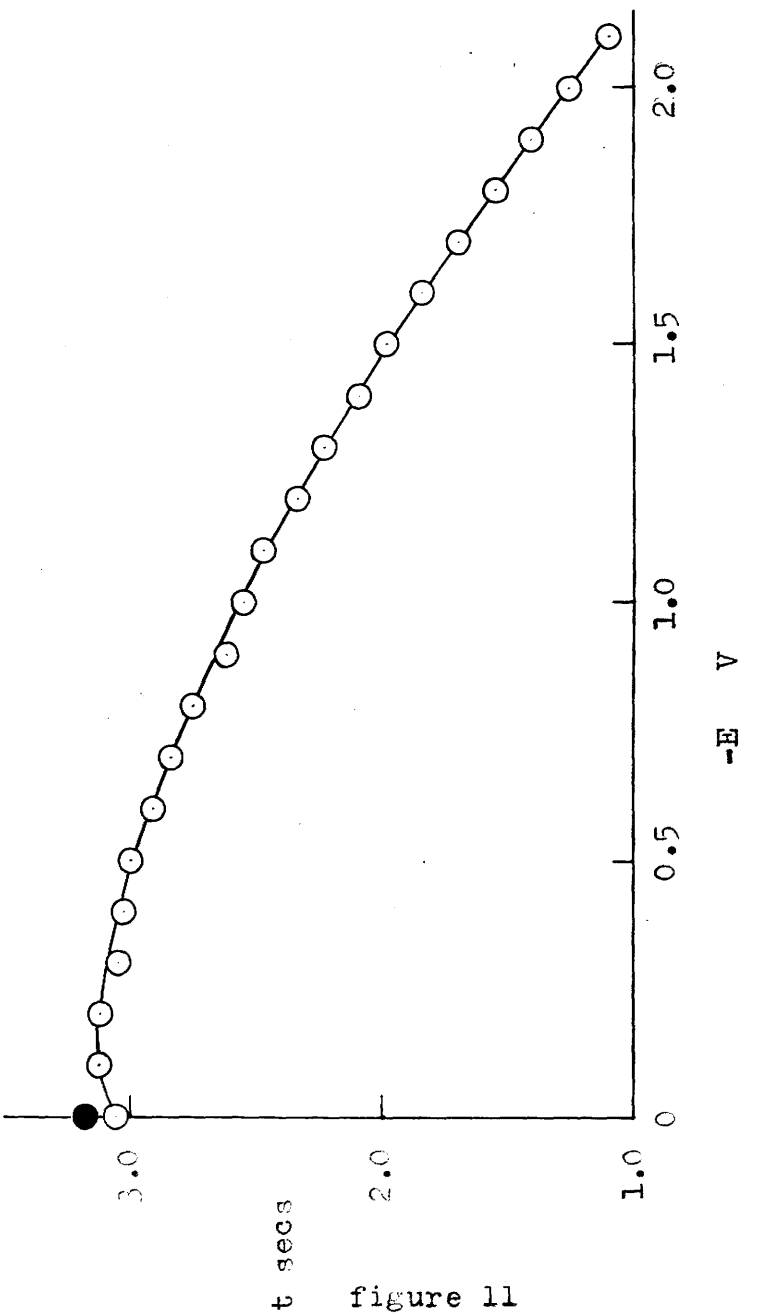


figure 11

Electrocapillarity curve.

RESULTS.

In general the hydrocarbons gave well defined waves. Some polarograms had maxima at concentrations over 1 mM, but these were invariably suppressed by dilution, and in some cases by the addition of a small amount of ethyl cellulose. Tangents were drawn to the portions of the waves with minimum and maximum slopes; and the $E_{\frac{1}{2}}$ values and diffusion currents (id) were evaluated for the points of intersection of these tangents. Within experimental error, ($\pm$ 5%) id was proportional to concentration in the range studied, (0.1 to 1 mM) but $E_{\frac{1}{2}}$ ($\pm$ 0.005 V) appeared in some cases to become slightly more negative at lower concentrations; often about 10 mV more negative at 0.3 mM than at 1 mM. When two or more waves occur with $E_{\frac{1}{2}}$ values separated by only about 0.1 V, the accuracy will be less, especially at potentials approaching -2.0 V. The accuracy is also less with very insoluble compounds, yielding waves with id less than 0.1 μA. The values of $E_{\frac{1}{2}}$ and $id/c.m^{\frac{2}{3}}t^{\frac{1}{6}}$ listed in Table 4 (pp. 95-101) are means of consistent determinations at a minimum of two concentrations (c). $E_{\frac{1}{2}}$ is expressed in V with respect to the mercury pool electrode in solution A; and for the compounds investigated also by Laitinen, Wawzonek, and Fan[81,82], or by Hoijtink and Van Schooten[87], the values here reported will be found to be about 0.5 V less negative than those obtained in

75% dioxan with respect to the saturated calomel electrode.

The $E_{\frac{1}{2}}$ values were assumed to be independent of acidity function[80], and no attempt was made to buffer the solutions. For a representative selection of polarographic waves, E was plotted against log id/(id-i). The rising part of the wave gave an approximation to a linear relationship in all cases, and the slope corresponded to the uptake of a single electron. This does not, however, prove that the reversible addition of a single electron is the only potential-determining step. (Aromatic nitro-compounds, whose $E_{\frac{1}{2}}$ values are undoubtedly pH-dependent and which are reduced irreversibly, gave slopes indicative of a single electron uptake in acetic acid[71] (see Part 1)).

The wave lengths of the p-bands, as classified and defined by Clar[92], of the hydrocarbons were in general obtained from "Aromatische Kohlenwasserstoffe"[93]. The values of the wave number ($\tilde{\nu}$) of the first (highest λ) p-band in the absorption spectra of the hydrocarbons are included in the table. Those that had been measured in benzene solution were, for comparative purposes, corrected to ethanol by the relationship:

$$\tilde{\nu}\ \text{ethanol} = \tilde{\nu}\ \text{benzene} + 300\ (\text{cm}^{-1})$$

which is characteristic of p-bands[92].

DISCUSSION.

When $E_{\frac{1}{2}}$ is plotted against π, (the number of π electrons per molecule) the results for various "annelation" series approximate to exponential curves (Figs.12 and 13). This is to be expected, for as the molecule grows longer, the electrons of the end ring will be further away from the centre of the molecule, where reduction will occur, and will have correspondingly smaller effect.

According to Wawzonek et al.[80] the potential-determining step in the polarographic reduction of conjugated systems is the reversible addition of one or more electrons. Maccoll[62] assumed that the added electron would enter the lowest unoccupied molecular orbital, and that the entropy change for the electron transfer would remain constant for the various aromatic species. Watson and Matsen[86] pointed out that the wave number $\tilde{\nu}$ of the absorption band representing the first permitted electronic transition would give the difference in energy between the highest occupied and the lowest unoccupied molecular orbital. There should, therefore, be a simple relationship between $\tilde{\nu}$ and $E_{\frac{1}{2}}$. Accordingly the $E_{\frac{1}{2}}$-values for the first reduction wave have been plotted against $\tilde{\nu}$ for the first p-band.

In general, the points lie very close to a straight

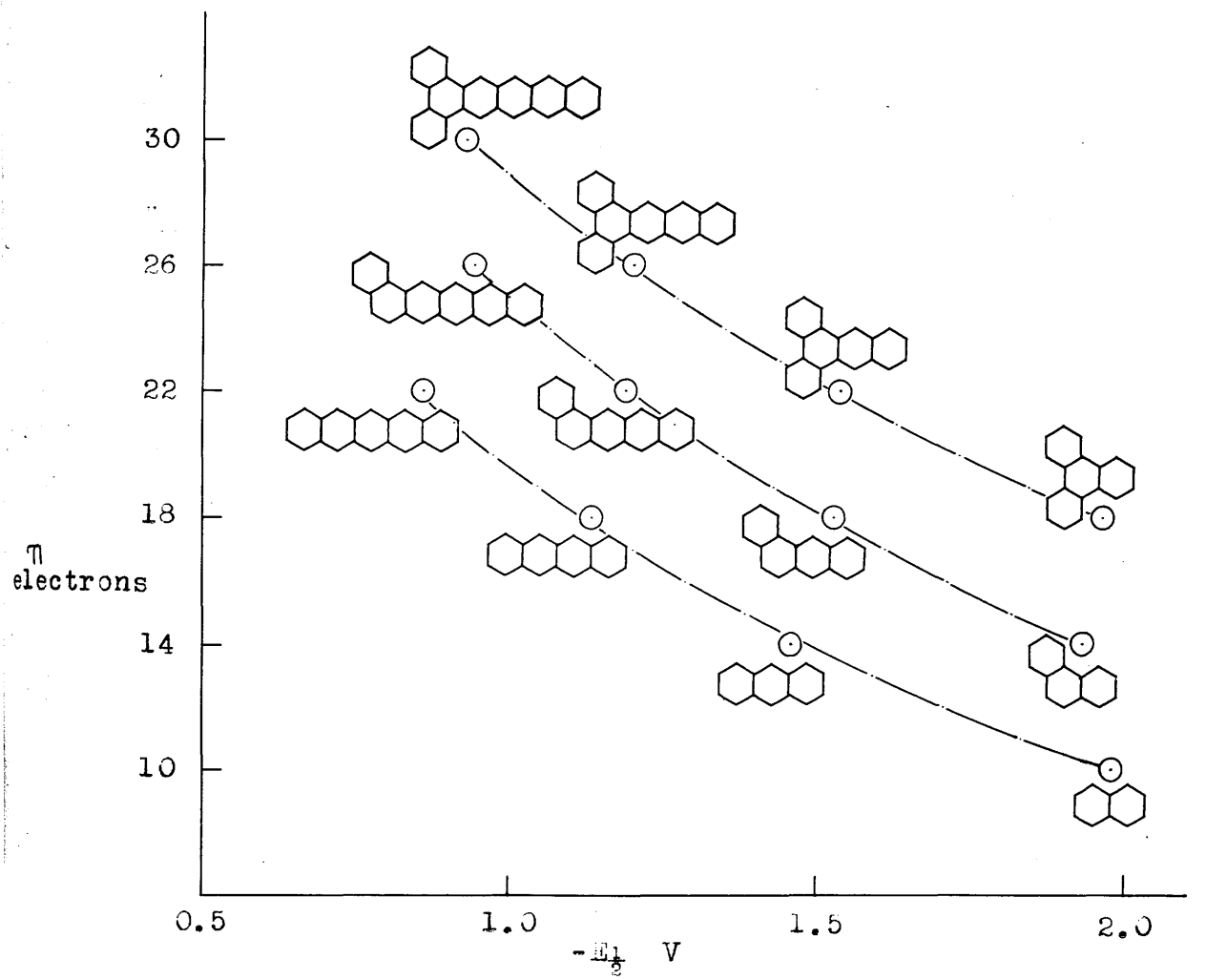


figure 12

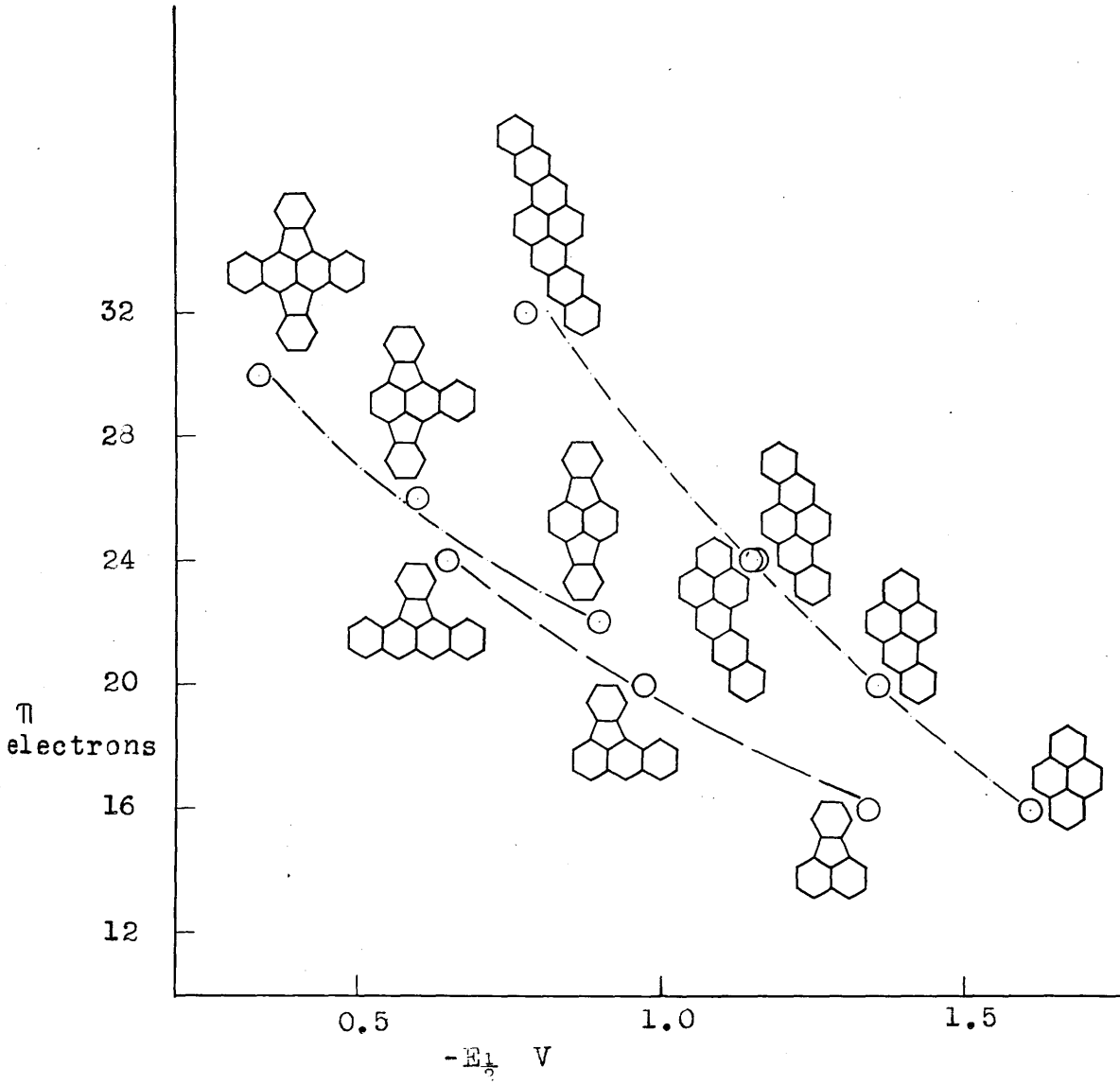


figure 13

line for each group of hydrocarbons, as shown in Figs.15 - 22. These groups are:

(a) the cata-condensed hydrocarbons, or "acenes" (I - XXXI),

(b) hydrocarbons related to perylene (XXXII - XLVIII),

(c) related to pyrene (XLIV - LXI),

(d) related to fluoranthene (LXII - LXIX)

(e) derived from dibenz-pyracylene (peri-phenylene-fluoranthene (LXX - LXXII).

The equations of these lines (see Fig.14) are:-

(a) $E_{\frac{1}{2}} = -0.62 \times 10^{-4}\tilde{\nu} + 0.20$

(b) $E_{\frac{1}{2}} = -0.78 \times 10^{-4}\tilde{\nu} + 0.56$

(c) $E_{\frac{1}{2}} = -0.635 \times 10^{-4}\tilde{\nu} + 0.28$

(d) $E_{\frac{1}{2}} = -0.705 \times 10^{-4}\tilde{\nu} + 0.63$

(e) $E_{\frac{1}{2}} = -0.67 \times 10^{-4}\tilde{\nu} + 0.735.$

When the wave numbers are replaced by the corresponding energies in electron-volts, the slopes ($\Delta E_{\nu} / \Delta E_{\frac{1}{2}}$) become: (a) 2.0, (b) 1.59, (c), 1.96, (d) 1.75, (e) 1.85, which are in satisfactory agreement with the value (2) predicted by Watson and Matsen[86] on the basis of Maccoll's relationship.

The poly-phenyls give a non-linear relationship in contrast to fluorene and benz-fluorene (LXXVI and LXXVII) which appear to behave similarly to group (a) (Fig.23). The 11.12-substituted fluoranthenes (LXVII and LXIX) appear

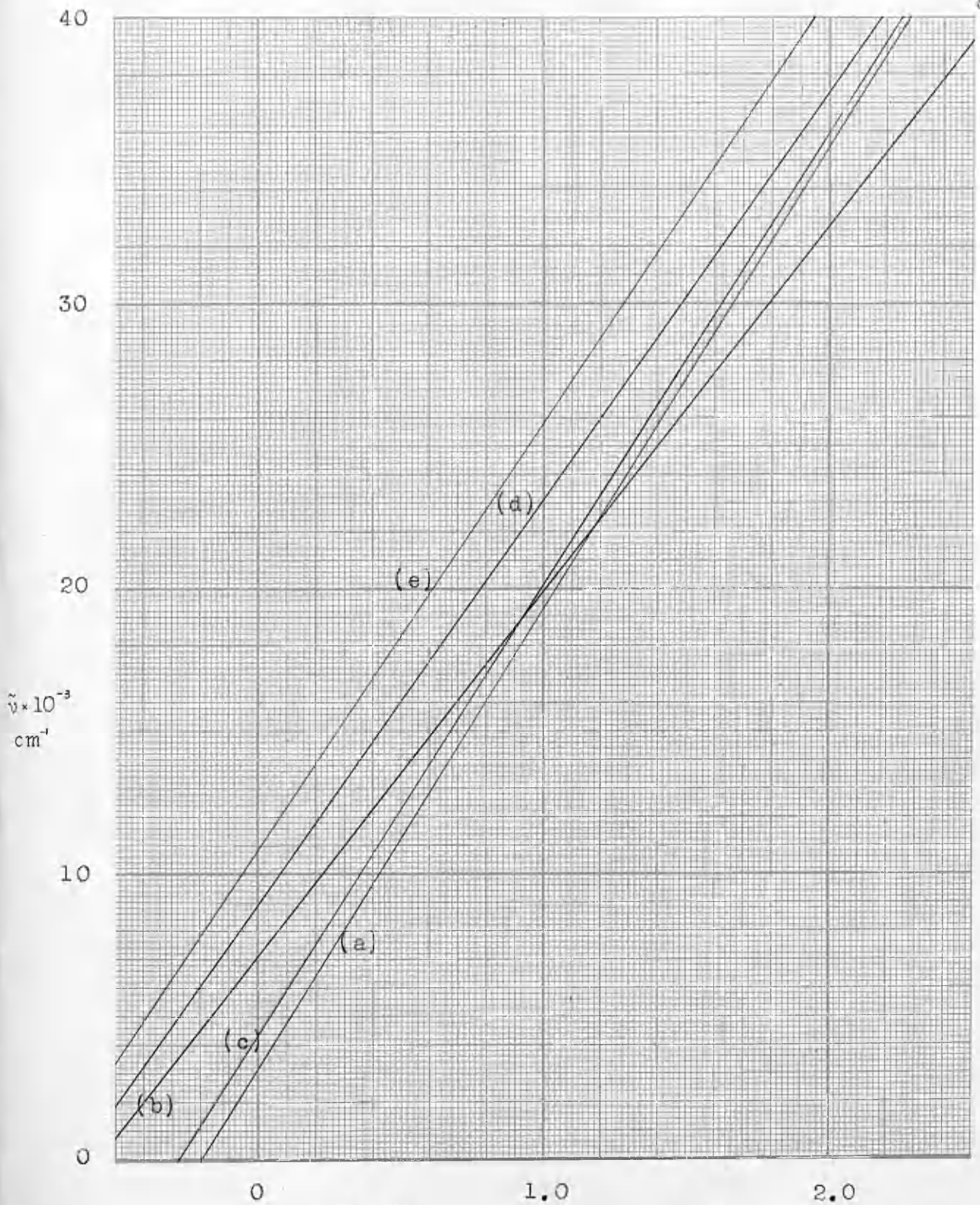


figure 14

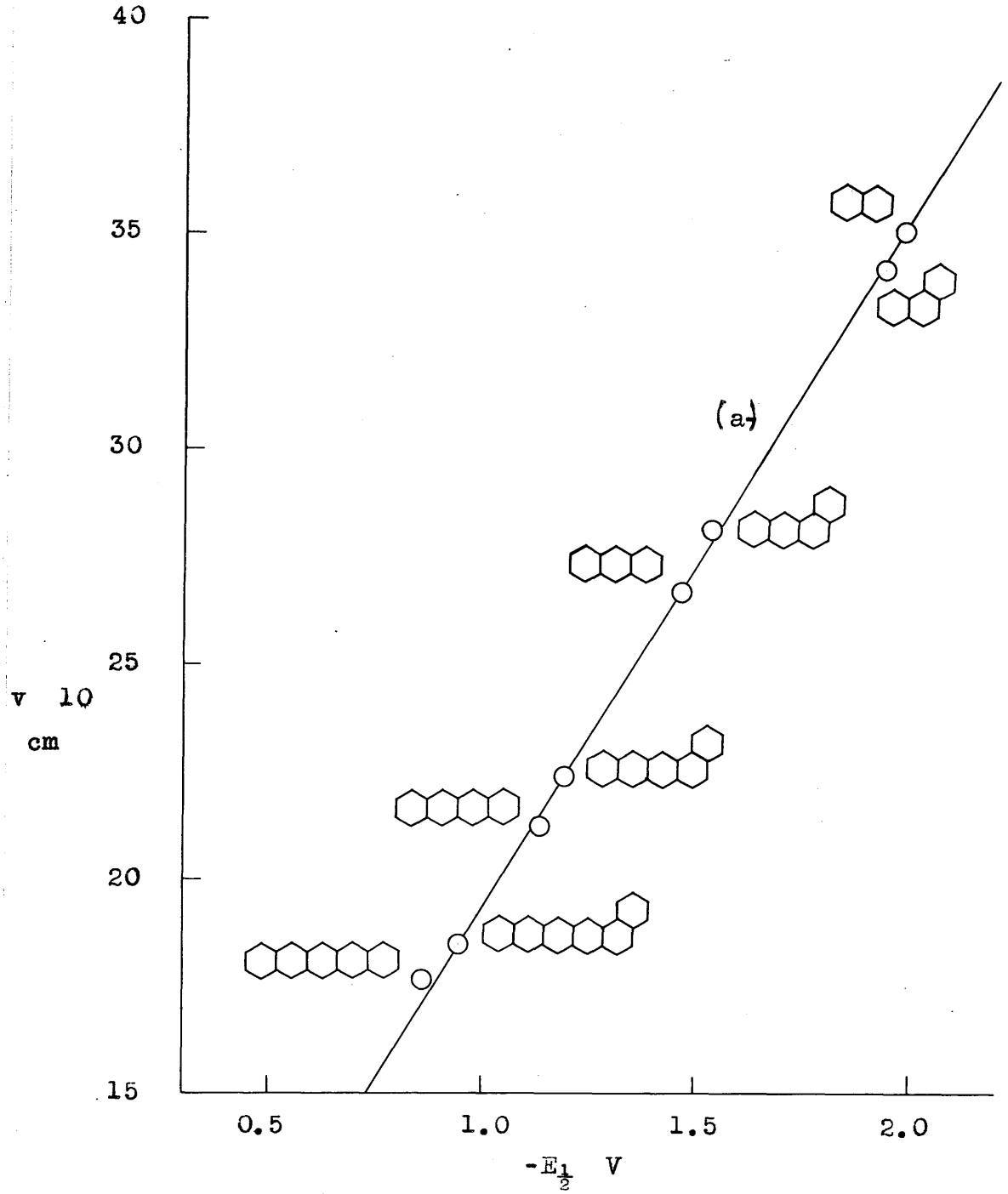


figure 15

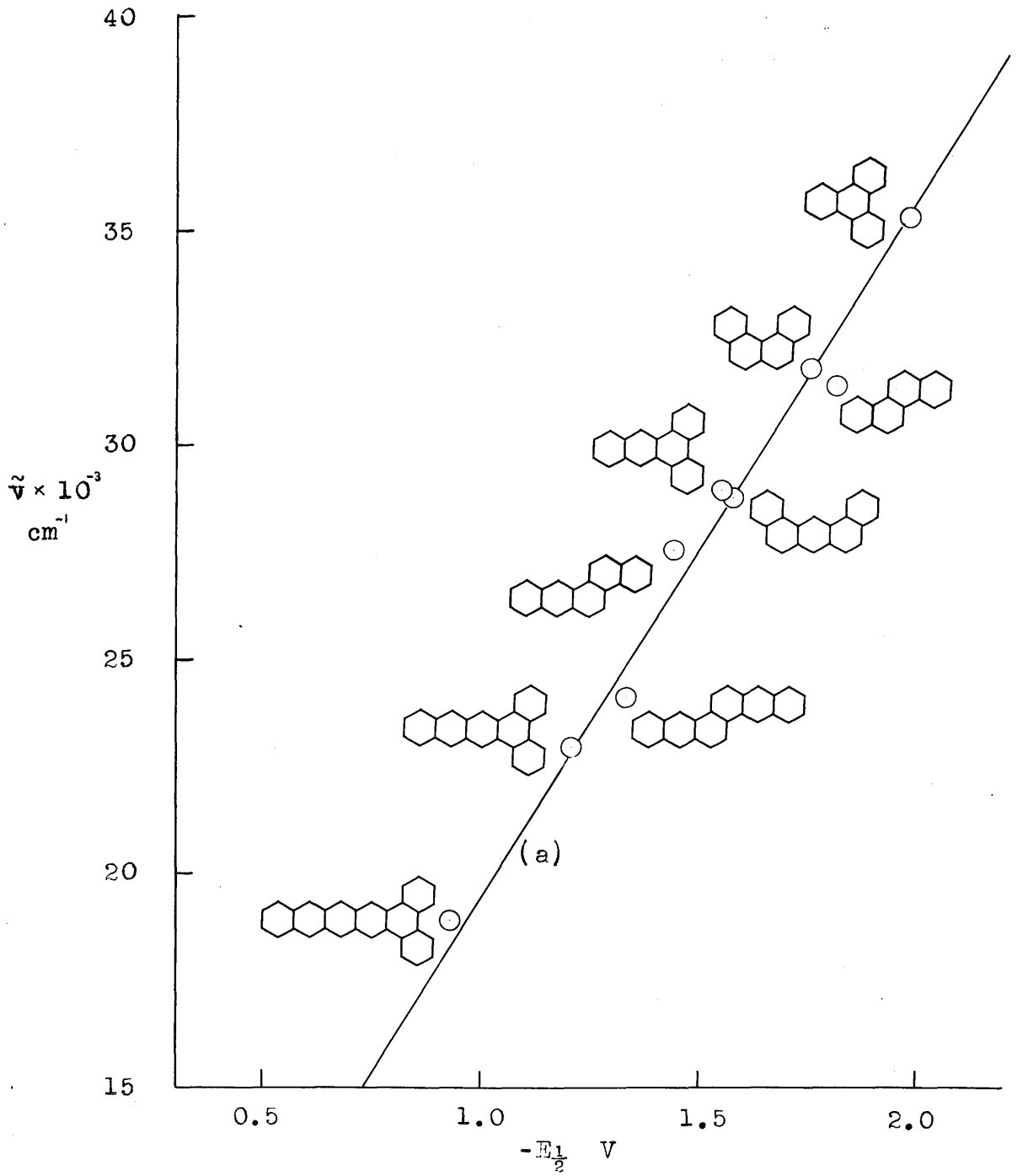


figure 16

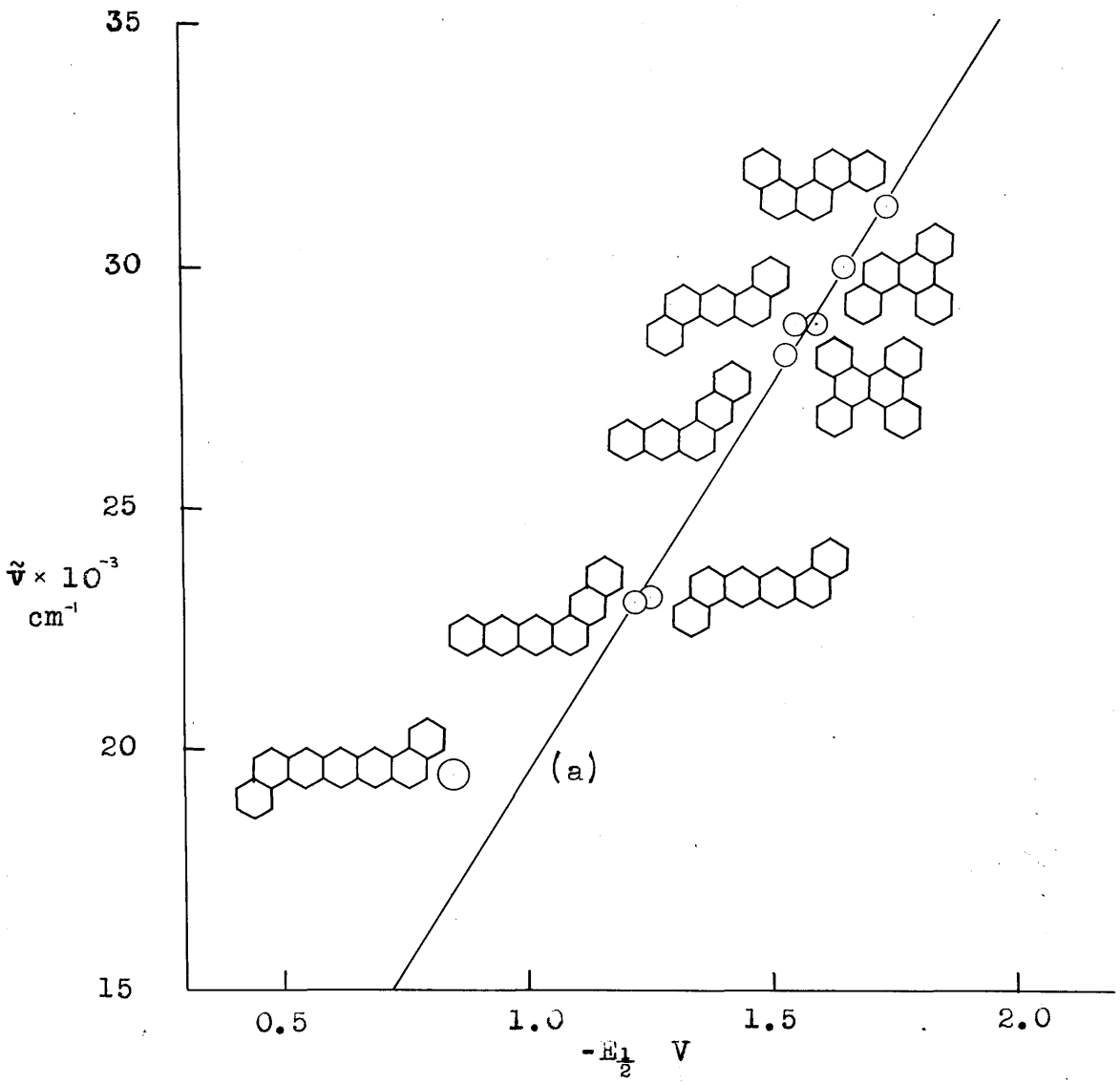


figure 17

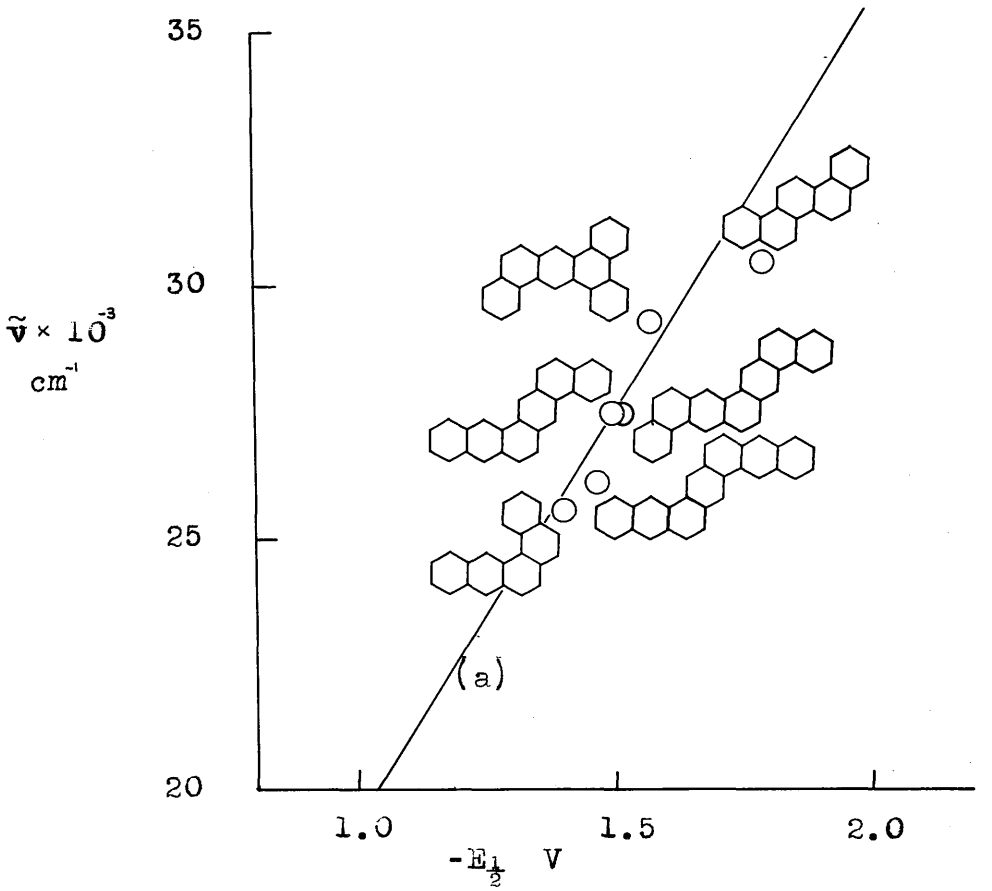


figure 18

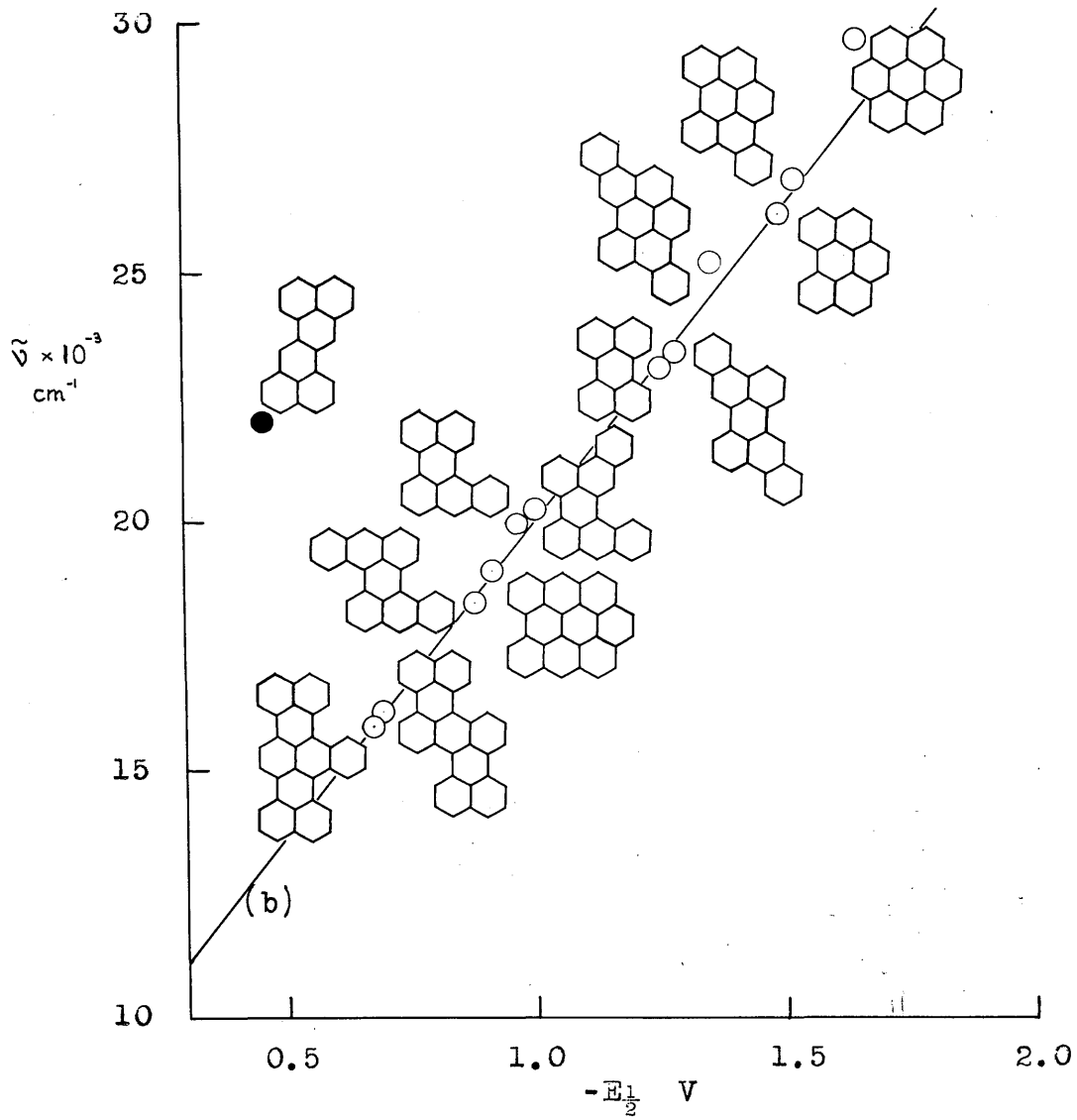


figure 19

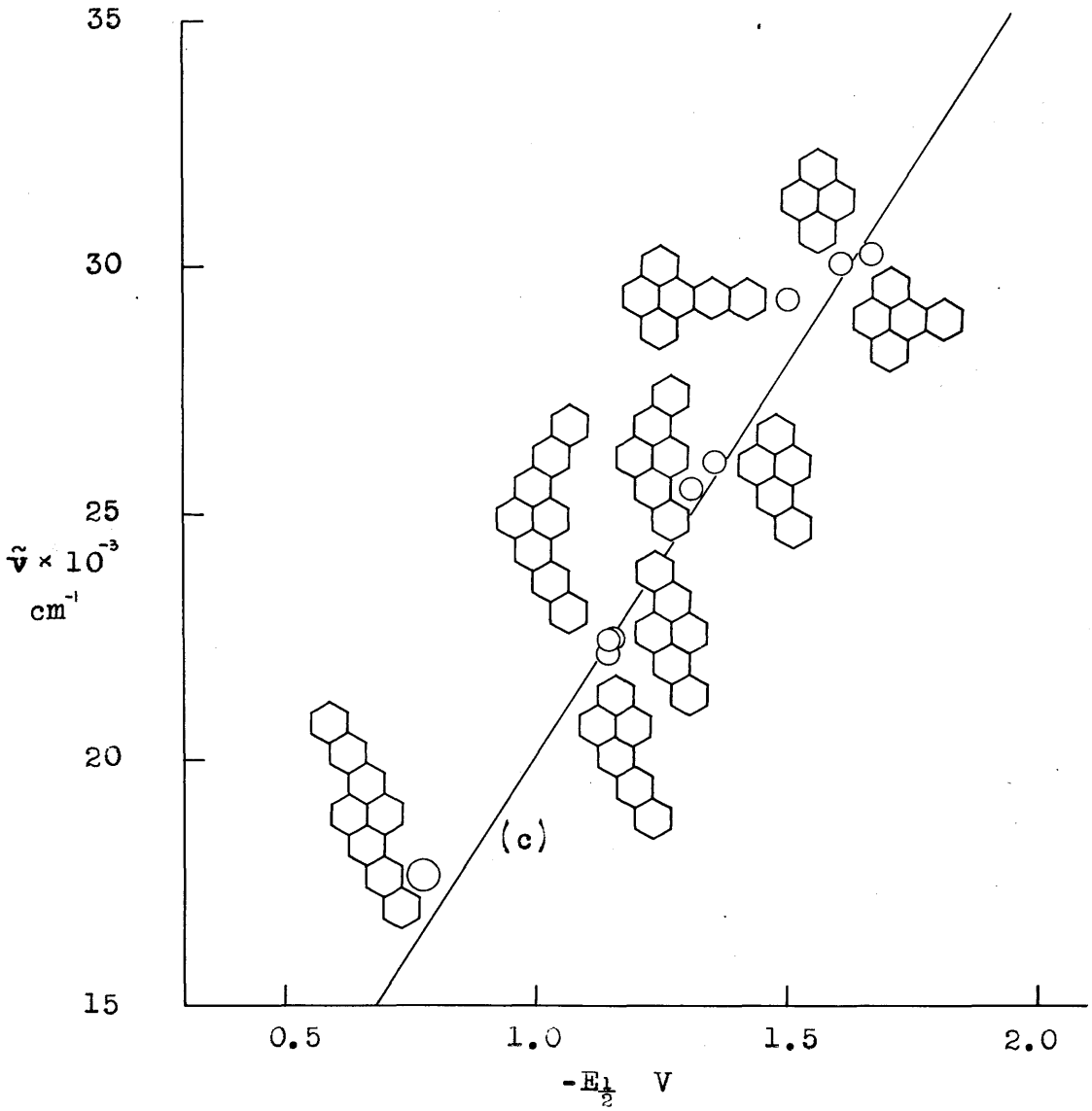


figure 20

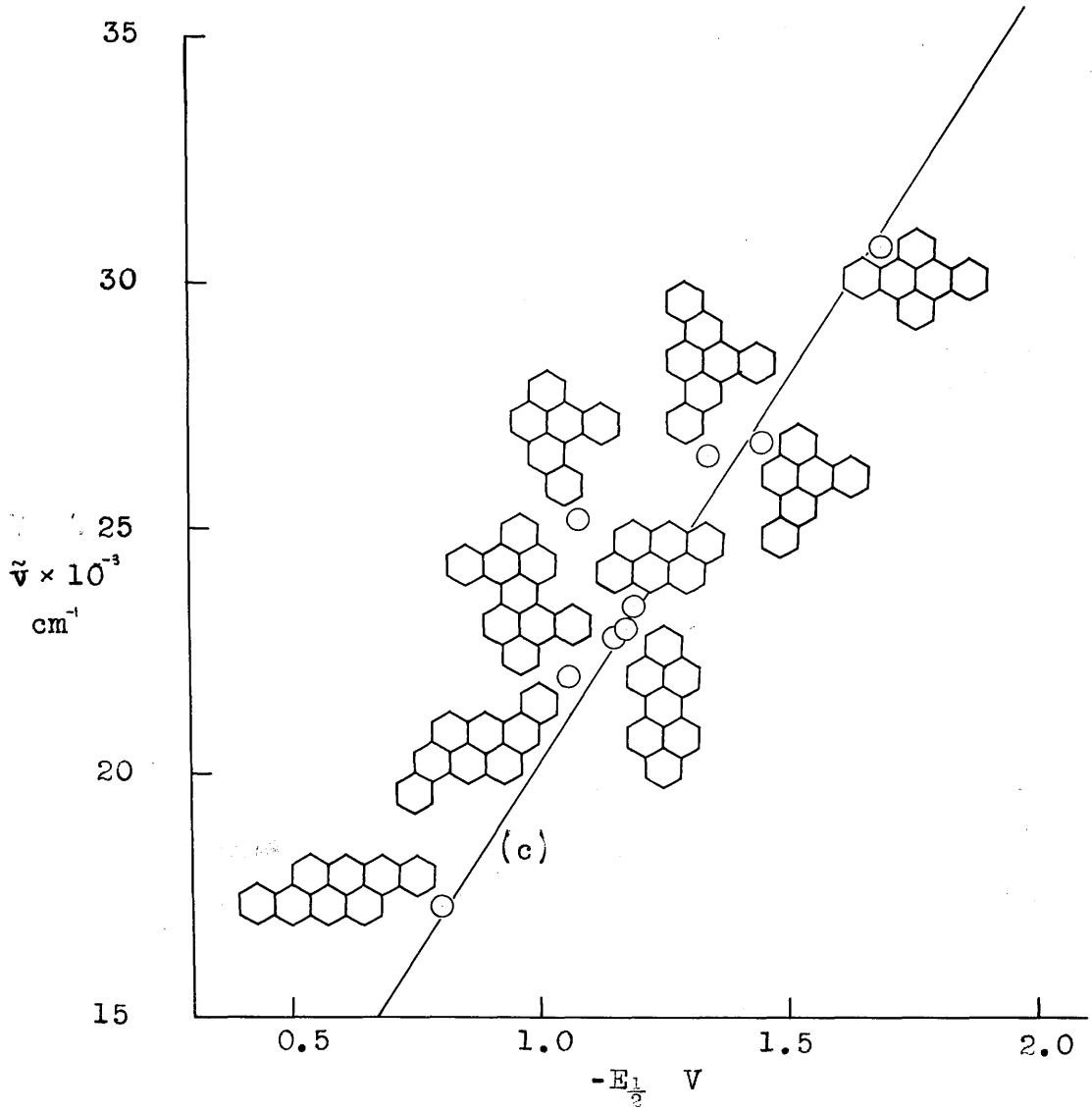


figure 21

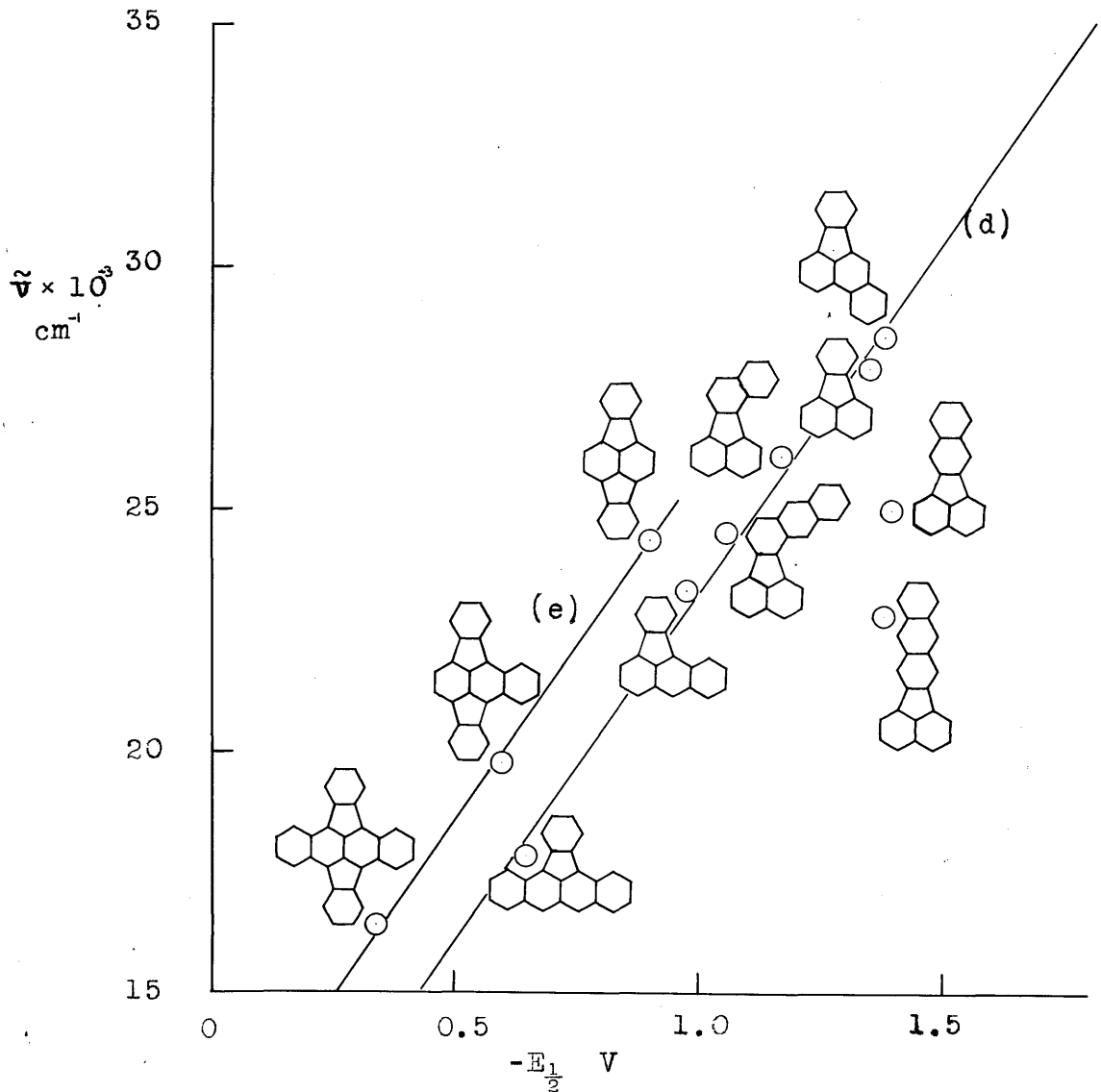


figure 22

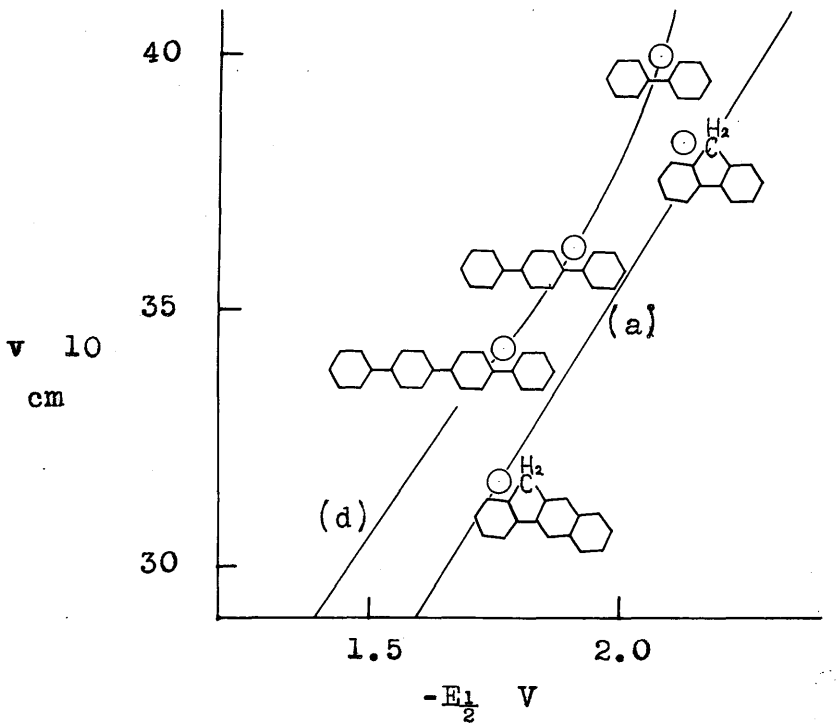
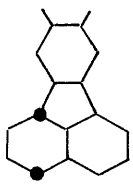


figure 23

to be anomalous (Fig.22). This is probably due to the changing over of the centres of reactivity from those characteristic of fluoranthenes,  to those in the 11.12-substituting naphthalene or anthracene residue.

1:2,3:4, dibenz-pyrene (XLVII) (Fig.21) appears to be more reactive than expected on the basis of its spectrum: this could be due to non planarity of the molecule. Coronene (XXXIX) (Fig.19) appears to resemble compounds related to pyrene, rather than those related to perylene according to the above relationship. Benzanthrene (LXXXI) appears among the perylenes according to the above scheme. Dibenzphenanthrene (LXXIX), despite its non-planarity, is reduced at a higher potential than expected. (Compounds Nos.LXXIX, LXXX and LXXXI do not appear in Figures 15 - 23).

The results for zethrene (LXXVIII) are given with the reservation that they represent the reduction of a compound whose $E_{\frac{1}{2}}$ will almost certainly vary with change in acidity function, in an unbuffered medium. The waves appeared normal, however, and are indicative of a very facile initial reduction, followed by a second wave characteristic of naphthalene residues. Zethrene in 98% acetic acid (1 M ammonium acetate) in which it is protonated, gave no wave. This fact may be related to the anomalously high $E_{\frac{1}{2}}$ values

of aromatic nitro-compounds which exist as cations in acetic acid[71] (see Part 1). A steric effect may exist, preventing the reactive centres in the molecule approaching the cathode surface to receive electrons.

No relationship was observed between $E_{\frac{1}{2}}$- values and α-absorption bands[92], which are, for many hydrocarbons, the series nearest the visible.

Table 4.

Substance		$E_{\frac{1}{2}}$	$id/c.m^{\frac{2}{3}}t^{\frac{1}{6}}$ **	$\tilde{\nu}$	Solvent
		V	$\mu A sec^{\frac{1}{2}}/mM.mgm^{\frac{2}{3}}$	cm^{-1}	
I		1.98	5.5	35090	ethanol
II		1.46	3.3	26700	ethanol
III	(a)	1.135	1.51	21230	ethanol
	(b)	2.02	1.47		
IV	(a)	0.86*	(0.053)	17380	benzene
	(b)	1.92	(0.094)		
V	(a)	1.935	3.4	34190	ethanol
	(b)	2.125	3.9		
VI	(a)	1.53	3.3	27860	benzene
	(b)	1.985	3.4		
VII	(a)	1.19	2.54	22100	benzene
	(b)	1.945	4.6		
VIII	(a)	0.945	2.8	18150	benzene
	(b)	1.64	2.7		
	(c)	1.96	1.03		
IX		1.97	8.84	35210	ethanol
X	(a)	1.54	2.8	28650	benzene
	(b)	1.995	5.55		
XI	(a)	1.205	1.65	22650	benzene
	(b)	1.51	1.45		
	(c)	1.98	6.8		
XII	(a)	0.93	1.88	18570	benzene
	(b)	1.95	9.44		
XIII	(a)	1.545	1.85	28490	benzene
	(b)	1.97	4.3		
XIV	(a)	1.25	1.8	22860	benzene
	(b)	1.745	4.7		
	(c)	1.935	6.2		
XV		ca. 0.85*	(0.04)	19120	benzene

Table 4 (Contd.)

Substance		$E_{\frac{1}{2}}$ V	$id/c.m^{\frac{2}{3}}t^{\frac{1}{6}}$ ** $\mu A sec^{\frac{1}{2}}/mM.mgm^{\frac{2}{3}}$	$\tilde{\nu}$ cm^{-1}	Solvent
XVI	(a)	1.805	5.5	31350	ethanol
	(b)	2.165	2.9		
XVII	(a)	1.435	2.55	27250	benzene
	(b)	1.88	2.45		
	(c)	2.15	3.5		
XVIII	(a)	1.33*	(0.2)	23810	benzene
	(b)	1.95	(0.2)		
XIX	(a)	1.745	4.8	31750	ethanol
	(b)	2.01	1.43		
XX	(a)	1.57	3.2	28490	benzene
	(b)	1.95	5.4		
XXI	(a)	1.645	2.6	29940	ethanol
	(b)	1.77	2.7		
	(c)	2.04	5.9		
XXII	(a)	1.57	2.35	28990	benzene
	(b)	1.97	8.1		
XXIII	(a)	1.59	2.35	28490+	benzene
	(b)	1.85	3.3		
	(c)	2.05	5.15		
XXIV		1.73	5.6	31200	ethanol
XXV	(a)	1.40	2.2	25580+	ethanol
	(b)	1.87	2.05		
XXVI	(a)	1.79	4.5	30440	$CHCl_3$
	(b)	1.97	3.25		
XXVII	(a)	1.525	3.05	27860	benzene
	(b)	1.975	1.5		
XXVIII	(a)	1.22	2.25	22730	benzene
	(b)	1.53	2.6		
	(c)	1.945	3.3		
XXIX	(a)	1.495	4.25	27170	benzene
	(b)	1.94	2.5		

Table 4 (Contd.)

Substance		$E_{\frac{1}{2}}$ V	$id/c.m^{\frac{2}{3}}t^{\frac{1}{6}}$ * $\mu A sec^{\frac{1}{2}}/mM.mgm^{\frac{2}{3}}$	$\tilde{\nu}$ cm^{-1}	Solvent
XXX	(a)	1.515	(0.36)	27170	benzene
	(b)	1.945	(0.47)		
XXXI	(a)	1.465	(0.65)	25810	benzene
	(b)	1.915	(0.17)		
XXXII	(a)	1.25	1.05	23040	ethanol
	(b)	1.51	1.5		
	(c)	1.74	2.05		
XXXIII	(a)	0.965	2.05	19920+	ethanol
	(b)	1.705	3.45		
XXXIV	(a)	0.88	1.2	18310	methanol
	(b)	1.11	1.9		
	(c)	1.35	1.22		
XXXV	(a)	1.00	2.85	19900	benzene
	(b)	1.725	2.05		
	(c)	1.99	4.8		
XXXVI	(a)	1.485	1.6	25810	benzene
	(b)	1.675	2.95		
	(c)	1.87	3.65		
XXXVII	(a)	1.515	1.45	26490	benzene
	(b)	1.76	3.05		
	(c)	2.15	3.2		
XXXVIII	(a)	1.35	(0.16)	24880	benzene
	(b)	1.945	(0.5)		
XXXIX	(a)	1.64	4.1	29280	benzene
	(b)	1.855	9.7		
	(c)	1.94	12.2		
XL	(a)	1.28	2.1	23070	benzene
	(b)	1.585	2.1		
	(c)	1.97	4.3		
XLI	(a)	0.915*	(0.3)	18670	benzene
	(b)	1.13	(0.54)		
	(c)	1.75	(1.1)		
	(d)	2.06	(0.0)		

Table 4 (Contd.)

Substance		$E_{\frac{1}{2}}$ V	$id/c.m^{\frac{2}{3}}t^{\frac{1}{6}}$ ** $\mu A sec^{\frac{1}{2}}/mM.mgm^{\frac{2}{3}}$	$\tilde{\nu}$ cm^{-1}	Solvent
XLII	(a)	0.675	(0.45)	15550	benzene
	(b)	1.00	(0.9)		
	(c)	1.21	(0.8)		
	(d)	1.62	(0.75)		
	(e)	1.895	(1.9)		
XLIII	(a)	0.695	(0.15)	15870 ++	benzene
	(b)	1.03	(0.15)		
	(c)	1.80	(0.4)		
	(d)	2.05	(0.26)		
XLIV	(a)	1.61	3.25	29990	ethanol
	(b)	1.7 app.	3.3		
	(c)	1.8 app.			
	(d)	2.12	4.05		
XLV	(a)	1.67	6.15	30170	ethanol
	(b)	2.025	3.55		
XLVI	(a)	1.36	2.15	26010	ethanol
	(b)	1.59	2.35		
	(c)	1.89	1.45		
XLVII	(a)	1.08	0.85	24880	benzene
	(b)	1.30	0.87		
	(c)	1.58	1.15		
	(d)	1.75	1.15		
	(e)	2.09	1.3		
XLVIII	(a)	1.445	2.1	26460	benzene
	(b)	1.71	2.3		
	(c)	2.08	3.5		
XLIX	(a)	1.685	7.45	30400	benzene
	(b)	2.01	4.15		
L	(a)	1.16	2.5	22170	benzene
	(b)	1.69	3.4		
	(c)	2.07	5.9		
LI	(a)	1.315	2.5	25190	benzene
	(b)	1.58	2.8		
LII	(a)	1.505	3.05	28990	benzene
	(b)	1.62	3.35		

Table 4 (Contd.)

Substance	$E_{\frac{1}{2}}$ V	$id/c.m^{\frac{2}{3}}t^{\frac{1}{6}}$ ** $\mu A sec^{\frac{1}{2}}/mM.mgm^{\frac{2}{3}}$	$\tilde{\nu}$ cm^{-1}	Solvent
LIII	(a) 1.15	2.2	21830	benzene
	(b) 1.59	4.55		
	(c) 2.01	5.45		
LIV	(a) 0.78*	(0.34)	17360	benzene
	(b) 1.18	(1.15)		
LV	1.15*	(0.115)	22120	benzene
LVI	(a) 1.34	2.15	26180	benzene
	(b) 2.10	8.9		
LVII	(a) 1.175	(0.38)	22910	ethanol
	(b) 1.38	(0.36)		
	(c) 1.965	(0.77)		
LVIII	(a) 1.15	(0.7)	22470	benzene
	(b) 1.375	(0.95)		
	(c) 1.57	(0.7)		
	(d) 1.70	(0.7)		
	(e) 1.78	(1.0)		
	(f) 2.01	(1.09)		
LIX	(a) 1.19	1.85	23090	benzene
	(b) 1.68	2.4		
	(c) 1.94	4.45		
LX	(a) 1.06*	(0.09)	21650	benzene
LXI	(a) 0.80*	(0.05)	16980	benzene
LXII	(a) 1.345	1.35	27890	ethanol
	(b) 1.64	2.1		
	(c) 2.10	2.9		
LXIII	(a) 0.975	1.45	23360	ethanol
	(b) 1.255	1.2		
	(c) 2.075	3.25		
LXIV	(a) 0.65	1.07	17510	benzene
	(b) 0.85	1.3		
	(c) 1.72	2.0		

Table 4 (Contd.)

Substance		$E_{\frac{1}{2}}$ V	$id/c.m^{\frac{2}{3}}t^{\frac{1}{6}}$ ** $\mu A sec^{\frac{1}{2}}/mM.mgm^{\frac{2}{3}}$	$\tilde{\nu}$ cm^{-1}	Solvent
LXV	(a)	1.375	1.65	28570	ethanol
	(b)	1.895	3.4		
LXVI	(a)	1.165	0.62	26110	ethanol
	(b)	1.45	1.2		
	(c)	1.815	1.0		
LXVII	(a)	1.39	1.65	25000	ethanol
	(b)	1.62	1.5		
	(c)	1.79	3.0		
LXVIII	(a)	1.055	1.2	24540+	ethanol
	(b)	1.35	4.3		
	(c)	1.87	2.05		
LXIX	(a)	1.375	3.5	22830	ethanol
	(b)	1.67	2.4		
	(c)	2.12	5.9		
LXX	(a)	0.90	1.1	24390	ethanol
	(b)	1.285	1.9		
	(c)	1.935	2.9		
LXXI	(a)	0.60	0.55	19490+	benzene
	(b)	0.97	1.0		
	(c)	1.25	0.47		
LXXII	(a)	0.34	(0.22)	16400	benzene
	(b)	0.695	(0.3)		
	(c)	1.855	(0.3)		
LXXIII		2.075	5.0	40000	ethanol
LXXIV	(a)	1.905	3.5	26230	hexanol
	(b)	2.13	3.7		
LXXV	(a)	1.765	2.7	34250	hexane
	(b)	1.90	2.75		
LXXVI		2.12	3.96	38310	ethanol
LXXVII		1.76	2.6	31640	ethanol
LXXVIII	(a)	0.46	(0.14)	21690	benzene
	(b)	2.09	(0.74) or	16080	benzene

Table 4 (Contd.)

Substance		$E_{\frac{1}{2}}$ V	$id/c.m^{2/3}t^{1/6}$ ** $\mu A sec^{1/2}/mM.mgm^{2/3}$	$\tilde{\nu}$ cm^{-1}	Solvent
LXXIX		1.75	6.15	30400	ethanol
LXXX	(a)	1.22	1.39	23000+++	ethanol
	(b)	1.44	1.04		
	(c)	1.74	2.8		
LXXXI		1.72	0.675	29070	ethanol.

* Solution B

** Figures in brackets refer to saturated solution, $id/m^{2/3}t^{1/6}$.

+ Ref. 94

++ Ref. 95

+++ Ref.96.

Table 4(a).

Polynuclear Aromatic Hydrocarbons.

I	Naphthalene
II	Anthracene
III	Tetracene
IV	Pentacene
V	Phenanthrene
VI	1.2-Benz-anthracene
VII	1.2-Benz-tetracene
VIII	1.2-Benz-pentacene
IX	Triphenylene
X	1.2,3.4-Dibenz-anthracene
XI	1.2,3.4-Dibenz-tetracene
XII	1.2,3.4-Dibenz-pentacene
XIII	1.2,5.6-Dibenz-anthracene
XIV	1.2,7.8-Dibenz-tetracene
XV	1.2,8.9-Dibenz-pentacene
XVI	Chrysene
XVII	Naphtho-(2'.1':1.2)-anthracene
XVIII	Anthraceno-(2'.1':1.2)-anthracene
XIX	3.4-Benz-phenanthrene
XX	1.2,7.8-Dibenz-anthracene
XXI	1.2-Benz-chrysene
XXII	1.2,3.4,5.6-Tribenz-anthracene
XXIII	1.2,7.8-Dibenz-chrysene
XXIV	5.6-Benz-chrysene
XXV	Naphtho-(1'.2':1.2)-anthracene
XXVI	Picene
XXVII	Pentaphene
XXVIII	Hexaphene
XXIX	3.4-Benzpentaphene
XXX	3.4,9.10-Dibenz-pentaphene
XXXI	Naphtho-(2'.3':3.4)-pentaphene
XXXII	Perylene
XXXIII	1.2-Benz-perylene
XXXIV	1.2,7.8-Dibenz-perylene
XXXV	1.2,10.11-Dibenz-perylene
XXXVI	1.12-Benz-perylene
XXXVII	1.12,2.3-Dibenz-perylene
XXXVIII	1.12,2.3,8.9-Tribenz-perylene
XXXIX	Coronene
XL	2.3,8.9-Dibenz-perylene
XLI	1.14-Benz-bisanthrene
XLII	7.8-Benz-terrylene
XLIII	1.9,4.5-Di-peri-naphthyl-anthracene

XLIV	Pyrene
XLV	1.2-Benz-pyrene
XLVI	3.4-Benz-pyrene
XLVII	1.2,3.4-Dibenz-pyrene
XLVIII	1.2,4.5-Dibenz-pyrene
XLIX	1.2,6.7-Dibenz-pyrene
L	3.4,8.9-Dibenz-pyrene
LI	3.4,9.10-Dibenz-pyrene
LII	Naphtho-(2'.3':1.2)-pyrene
LIII	Naphtho-(2'.3':3.4)-pyrene
LIV	Dinaphtho-(2'.3':3.4),(2".3":8.9)-pyrene
LV	Dinaphtho-(2'.3':3.4),(2".3":9.10)-pyrene
LVI	1.2,3.4,5.6-Tribenz-pyrene
LVII	Peropyrene
LVIII	4.5,11.12-Dibenz-peropyrene
LIX	Anthrathrene
LX	1.2,7.8-Dibenz-anthrathrene
LXI	2.3,8.9-Dibenz-anthrathrene
LXII	Fluoranthene
LXIII	2.3-Benz-fluoranthene
LXIV	2.3,6.7-Dibenz-fluoranthene
LXV	3.4-Benz-fluoranthene
LXVI	10.11-Benz-fluoranthene
LXVII	11.12-Benz-fluoranthene
LXVIII	Naphtho-(2'.3':10.11)-fluoranthene
LXIX	Naphtho-(2'.3':11.12)-fluoranthene
LXX	peri-Phenylene-fluoranthene (Dibenz-pyracylene)
LXXI	Isorubicene
LXXII	5.6,11.12-Diphenylene-tetracene
LXXIII	Diphenyl
LXXIV	Terphenyl
LXXV	Quaterphenyl
LXXVI	Fluorene
LXXVII	2.3-Benz-fluorene
LXXVIII	Zethrene
LXXIX	3.4,5.6-Dibenz-phenanthrene
LXXX	2.3-Benz-perylene
LXXXI	Benzanthrene.

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CONCLUSION.

It has been shown that cathodic reduction studies may be related to the structure of molecules and their electronic distribution. In conjunction with other physico-chemical data this method may yield much information about reactivity and reaction mechanisms.

It is hoped to extend the work described in Part 3 by the study of compounds which are likely to be intermediates in the reduction of hydrocarbons. A micro reduction cell with quartz windows has been constructed. This will be used to study the products of reduction of some hydrocarbons at a stirred mercury surface, both by coulometry and by spectrophotometry. It is hoped in this way to prepare reduction products otherwise unobtainable.